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(54) LOW MOLECULAR WEIGHT ETHYLENE-BASED POLYMER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject polymer containing a specific unsaturated bond at the one side terminal of the polymer chain and useful for the production of a releasing agent for a toner, a pigment-dispersing agent, and a lubricant for the molding of a vinyl chloride resin by polymerizing ethylene singly or ethylene with a specific α -olefin by using a specific catalyst.

SOLUTION: The objective polymer having a vinyl type or a vinylidene type unsaturated bond at the one side terminal of the polymer chain consists of ethylene singly or ethylene and a 3-10C α -olefin and which satisfies (1) the content ratios of the ethylene unit and the α -olefin unit are 81-100 mol% and 0-19 mol% range, respectively, and (2) its intrinsic viscosity $[\eta]$ measured at 135° C in decalin is 0.01-1.7 dl/g, (3) its molecular weight distribution (Mw/Mn) measured by GPC is ≤ 3 and (4) its number of vinyl groups M and number of vinylidene groups N per 1,000 carbon atoms measured by an infrared absorption method satisfy a relational formula: $M+N \geq 14,000/M_w$.

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CLAIMS

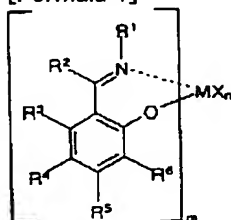
[Claim(s)]

[Claim 1] The unsaturated bond of a vinyl mold or a vinylidene mold is included in the single-sided end of a polymer chain. It is the low-molecular-weight polymer which consists of ethylene independence or ethylene, and an alpha olefin of carbon numbers 3-10. (1) A 81 - 100-mol % and alpha olefin unit has an ethylene unit in the 0 - 19-mol range of %. (2) The limiting viscosity $[\eta]$ measured in 135-degree-C decalin is 0.01 - 1.7 dl/g. (3) — several vinyl groups per [which the molecular weight distribution (Mw/Mn) measured by GPC are three or less, and measured by (4) infrared absorption spectrometry] 1000 carbon — M and vinylidene — the base — the low-molecular-weight ethylene system polymer with which N is characterized by filling the following relational expression (I).
 $M+N \geq 14000/Mw$ (I)

[Claim 2] The low-molecular-weight ethylene system polymer with which an oxygen content radical, a nitrogen content radical, a boron content radical, a sulfur content radical, the Lynn content radical, the silicon content radical, the germanium content radical, the halogen content radical, or the tin content radical was combined with the end of one side of the polymer chain of a low-molecular-weight ethylene system polymer according to claim 1.

[Claim 3] (A) The transition-metals compound expressed with the following general formula (II), and (B) (B-1) Organometallic compound, (B-2) an organic aluminum oxy compound — and (B-3) According to the catalyst for olefin polymerization characterized by consisting of at least one sort of compounds chosen from the compound which reacts with a transition-metals compound (A) and forms an ion pair Ethylene independence or the low-molecular-weight ethylene system polymer according to claim 1 obtained by carrying out the polymerization of the alpha olefin of carbon numbers 3-10 to ethylene.

[Formula 1]



... (II)

(M shows the transition-metals atom of the 3-11th groups of a periodic table among a formula. m) The integer of 1-6 is shown, and even if R1-R6 are mutually the same, you may differ. A hydrogen atom, a halogen atom, a hydrocarbon group, heterocyclic compound residue, an oxygen content radical, A nitrogen content radical, a boron content radical, a sulfur content radical, the Lynn content radical, a silicon content radical, A germanium content radical or a tin content radical may be shown, it may connect mutually [two or more pieces] of these, and the ring may be formed. Two radicals may be connected among the radicals shown by R1-R6 when m is two or more. Moreover, n It is the number which fills the valence of M. X A hydrogen atom, a halogen atom, a hydrocarbon group, An oxygen content radical, a sulfur content radical, a nitrogen content radical, a boron content radical, an aluminum content radical, The Lynn content radical, a halogen content radical, heterocyclic compound residue, a silicon content radical, a germanium content radical, or a tin content radical is shown, and when n is two or more it may join together mutually and two or more radicals which may differ even if two or more radicals shown by X are mutually the same, and are shown by X may form a ring.

[Claim 4] The release agent for toners containing a low-molecular-weight ethylene system polymer according to claim 1 or 2.

[Claim 5] The pigment agent containing a low-molecular-weight ethylene system polymer according to claim 1 or 2.

[Claim 6] Lubricant for vinyl chloride resin containing a low-molecular-weight ethylene system polymer according to claim 1 or 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a new low-molecular-weight ethylene system polymer, the polymer permuted by the still more detailed functional group predetermined in the end of one side of a polymer chain, and its application. It is related with the application to the ethylene system polymer which becomes the single-sided end of a polymer chain from the specific molecular weight and the presentation which have the unsaturated bond of a vinyl mold or a vinylidene mold in more detail and its release agent for toners, a pigment agent, and the lubricant for vinyl-chloride-resin shaping.

[0002]

[Background of the Invention] (Low-molecular-weight ethylene system polymer) A low-molecular-weight ethylene system polymer belongs to the category of polyethylene (PE) oligomer. Polyethylene oligomer is also called a polyethylene system wax and is divided roughly into an animals-and-plants system, a mineral system, a petroleum-refining system, and a synthetic system. As a polyethylene system wax containing a functional group, the montanoic acid wax of a mineral system is mentioned to the single-sided end of a polymer chain. However, since a montanoic acid wax is extracted and refined from natural brown coal, its manufacturing cost is high. Moreover, in the montanoic acid wax, molecular weight was limited to about about 800 (dimer), what is a carboxylic acid or its ester was main, and the end of a polymer chain had few classes about what has other functional groups.

[0003] The system which used the metallocene catalyst is mentioned as a synthetic system which makes possible the cheap manufacturing cost of a polyethylene system wax. However, by such system, although a vinyl group can be introduced into the end of one side of a polymer chain, in order to lower the molecular weight of a polymer, the activity of chain transfer agents, such as hydrogen, is needed. Since the end of the polymer generated by this chain transfer agent was saturated, it had the problem that the number of single-sided end vinyl groups of the polymer chain which enables installation of other functional groups decreased extremely.

[0004] If it considers as the synthetic system which makes possible the cheap manufacturing cost of a polyethylene system wax, the system which pyrolyzes and low-molecular-weight-izes compound polyethylene is also mentioned. However, in this case, although there were more rates which an end vinyl group produces than the system which uses a metallocene catalyst system, in addition, they were still inadequate.

[0005] Also in any of the high voltage radical method which is a general-purpose synthetic approach, or a Ziegler catalyst method, it was difficult for a vinyl group to hardly exist in the end of the polymer chain obtained upwards, and to introduce an end vinyl group to a polymer chain intentionally.

[0006] (Release agent for toners) In electrostatic electrophotography, the development material for electrophotography and the so-called electrostatic toner develop the latent image formed of electrification exposure, and they are used in order to form a visible image. An electrostatic toner contains the electrification impalpable powder which makes it come to distribute coloring agents, such as carbon black and a pigment, in resin. It is divided roughly into the dry type binary system toner using electrification impalpable powder and carriers, such as iron powder and a glass particle, as [both] an electrostatic toner and the wet toner which distributed electrification impalpable powder with organic solvents, such as isoparaffin, and the dry type one component system toner with which magnetic impalpable powder was distributed.

[0007] By the way, the image which developed directly the image which was made to develop negatives on a photo conductor using an electrostatic toner, and was obtained in the paper in which the sensitization layer was formed after paper imprinted, and was obtained remains as it is, and it is fixed to it by heat or the solvent steam. Since the fixation by using a heating roller especially is a method of establishing a contact mold, thermal efficiency is high, and it has the advantages, like when an image can be comparatively established certainly also according to a low-temperature heat source, it is suitable also for the high-speed copy.

[0008] In recent years, in addition to a monochrome system photograph, the utilization range of color electrophotography spreads and the need of fixing an image under low energy is increasing increasingly. Reduction of the power consumption in the heating roller section used for fixation is required as the advance to the domestic appliance and small device of a copying machine for photographs progresses, and also the demand fixable [high-speed] required of the printing terminal of high-speed devices, such as a computer, is increasing. However, when contacting heating objects, such as a heating roller, fixing an image and the conventional electrostatic toner is used, the phenomenon imprinted by the image part to which the part adheres and follows a heating object, and the so-called offset phenomenon may arise. Since an electrostatic toner cannot fully become soft especially depending on

this heating when the temperature of a heating roller is low, it is easy to cause the fixable lowering to the print form and film of a toner in an offset phenomenon and coincidence. Especially, wax addition etc. is required, in a difficult existing color copying machine and a difficult existing color printer, prevention of offset generating makes a roller front face carry out impregnation of the silicone oil, or supplies silicone oil to a roller front face, for example, and the dissolution of an offset phenomenon is in drawing. However, technical problems, such as need, have occurred [the periodical supplement of silicone oil which cannot miniaturize the device by which the roller itself becomes dirty in this case, and by which the obtained image glares].

[0009] Various kinds of thermoplastics is used as a binder which is the principal member of an electrostatic toner. Electrification nature has good aromatic series system polyester resin which used styrene and (meta) an acrylic ester copolymer, a BIS-phenol A derivative, or a phthalic acid of low molecular weight etc. also especially in these thermoplastics, Hygroscopicity is [that fixable is good since it has suitable softening temperature (before or after 100 degrees C).] small, When that miscibility with carbon black and the pigment which are a coloring agent is good, it being easy to grind, and the resin concerned adhere to a photo conductor, washing of this photo conductor is easy and it has the features, like there is little contamination and it ends. However, also in said conventional electrostatic toner, since it is required that it should be the Sharp melt more and a fluid high resin design should be carried out from a viewpoint of colorization and the image nature maintenance in that case, it is difficult to prevent offset generating in a large fixation temperature requirement.

[0010] In order to solve such a problem, adding a polyolefine wax as a release agent in the conventional electrostatic toner was proposed (JP,52-3304,B, a 52-3305 official report, a 57-52574 official report, a 58-58664 official report, JP,58-59455,A), and it has put in practical use in the electrostatic toner for monochrome. However, it was difficult to raise an elevated-temperature mold-release characteristic, and to raise low-temperature fixable one.

[0011] (Pigment agent) As an approach of coloring synthetic resin, such as polystyrene, ABS, a polycarbonate, polyester, and a polyamide, the dry color method or the Colorcon pound method is mainly adopted, and the masterbatch method in which distributed mixing is promptly possible was seldom adopted. Also in which approach, in order to make synthetic resin distribute a pigment to homogeneity, the pigment agent is used. In the former, various metal salt [of higher fatty acids, such as stearin acid,], low-molecular-weight-polystyrene, and styrene-acrylic ester copolymerization oligomer etc. is used as a pigment agent for these synthetic resin. However, when these were used as a pigment agent, the pigment etc. carried out bleed out from the polymer obtained, the dispersibility of a pigment fell and there was a fault of the transparency of a polymer falling. Moreover, when low-molecular-weight polyolefine was used as a pigment agent, in the dry color method, in case a dry color is prepared, or when carrying out kneading preparation of this dry color for example, at a styrene system polymer, there was a problem that kneading workability fell, and there was also a fault that the pigment dispersibility of the polymer obtained further was also inferior. moreover — since homogeneity cannot be made to distribute a lot of pigments to the above-mentioned synthetic resin when said pigment agent is used — a masterbatch (MB) — it was difficult to adopt law.

[0012] On the other hand, in the coloring of polyolefin resin, such as polyethylene and polypropylene, and polyvinyl chloride resin, many masterbatch methods with possible making high concentration distribute a pigment in the resin of polyethylene and others using dispersants, such as low molecular weight polyethylene and fatty-acid metallic soap, are used. However, by the conventional masterbatch method, pigment concentration was not able to be made not much high. In recent years, a high dilution scale factor and high-speed coloring tend to be required, and, as for coloring of the synthetic resin of a polyolefine system or others, response sufficient by the conventional masterbatch method is becoming difficult. Especially, in the ***** type injection-molded product, since the distributed rate of the dyes and pigments to the inside of the ***** resin of a masterbatch was inadequate, the problem of a poor appearance, such as an irregular color of mold goods, was not avoided.

[0013] (Lubricant for vinyl chloride resin) Polyvinyl chloride resin has very bad thermal stability, and since the pyrolysis temperature of resin itself is below fabricating-operation temperature, the fabricating operation of resin is performed, being accompanied by the pyrolysis. Therefore, a lot of heat-resistant stabilizers for controlling degradation of resin and lubricant are needed for polyvinyl chloride resin. Although it is known well that the organic compound containing lead, cadmium, barium, etc. and the inorganic compound are excellent as a heat-resistant stabilizer of polyvinyl chloride resin conventionally, there are also metallic compounds which the activity of the above-mentioned heavy metal compound is restricted by the regulation on food sanitation hygiene or labor environment, and have come to be forbidden to inside. Therefore, the octyl tin considered that there is little toxicity, a lime compound, a zinc compound, etc. are beginning to be used as a heat-resistant stabilizer. However, since these stabilizers are inferior in a stabilizing effect and the slippage effectiveness compared with the conventional lead system stabilizer etc., it is necessary to compensate such effectiveness with lubricant. There are resin and compatibility in lubricant, plasticization of resin is brought forward, and it is divided roughly into external lubricant with the work (melting slippage) which prevents adhesion between resin and a metal the internal lubricant which reduces melt viscosity, and within an extruder at the time of mixing or melting, reduces frictional resistance, and raises workability, or the work (fine-particles slippage) which delays plasticization (henceforth gelation). As internal lubricant, butyl stearate, glycerol monostearate, etc. are mentioned, for example. As external lubricant, stearin acid, calcium stearate, etc. are mentioned, for example. As a thing which delays gelation among other external lubricant and which works, namely, has initial slippage, although paraffin wax, a micro crystallin wax, polyethylene wax, etc. are known, the adhesive prevention effectiveness over a metal side does not show the satisfactory engine performance. Furthermore, as external lubricant, a rice bran wax, oxidization polyethylene wax, its ester wax ghost and its metal

chloride, stearin acid, monoglyceride, etc. are known. However, although these have the prevention effectiveness to adhesiveness, there is little work which delays gelation.

[0014]

[Objects of the Invention] The molecular weight distribution of this invention is narrow, and it manufactures the low-molecular-weight ethylene system polymer which contained the functional group at the single-sided end of a polymer chain, and aims at offering the toner release agent excellent in an elevated-temperature mold-release characteristic and low-temperature fixable one, the pigment agent whose pigment dispersibility improved, and the outside lubricant for vinyl chloride resin which was excellent in initial slippage.

[0015]

[Summary of the Invention] The low-molecular-weight ethylene system polymer concerning this invention includes the unsaturated bond of a vinyl mold or a vinylidene mold in the single-sided end of a polymer chain. It is the low-molecular-weight polymer which consists of ethylene independence or ethylene, and an alpha olefin of carbon numbers 3-10. (One) ethylene unit 81 - 100-mol %, It is [limiting viscosity eta] 0.01-1.7 which an alpha olefin unit is in the 0-19-mol range of %, and measured in (2) 135-degree-C decalin. (3) — several vinyl groups per [which the molecular weight distribution (Mw/Mn) measured by GPC are three or less, and measured by (4) infrared absorption spectrometry] 1000 carbon — M and vinylidene — the base — N is characterized by filling the following relational expression (I).

[0016]

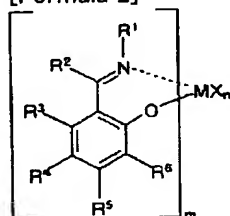
$$M+N \geq 14000/Mw \text{ (I)}$$

As for the low-molecular-weight polymer concerning this invention, an oxygen content radical, a nitrogen content radical, a boron content radical, a sulfur content radical, the Lynn content radical, a silicon content radical, a germanium content radical, a halogen content radical, or a tin content radical is permuted by the end (namely, end including the unsaturated bond of a vinyl mold or a vinylidene mold) of one side of the polymer chain of the above-mentioned low-molecular-weight ethylene system polymer by association (denaturation).

[0017] The transition-metals compound by which the low-molecular-weight polymer concerning this invention is expressed with the (A) following general formula (II), (B) (B-1) Organometallic compound (B-2), organic aluminum oxy compound, It reaches (B-3). According to the catalyst for olefin polymerization characterized by consisting of at least one sort of compounds chosen from the compound which reacts with a transition-metals compound (A) and forms an ion pair It is manufactured by carrying out the polymerization of the alpha olefin of carbon numbers 3-10 to ethylene independence or ethylene.

[0018]

[Formula 2]



... (II)

[0019] The release agent for toners concerning this invention consists of a low-molecular-weight ethylene system polymer with which the above ends may denaturalize. This release agent is used as a component of the toner for electrostatic-charge image development with an electrification control agent etc. binding resin (a), a coloring agent (b), and if needed, and contributes to the improvement in an elevated-temperature mold-release characteristic and low-temperature fixable.

[0020] The pigment agent concerning this invention consists of a low-molecular-weight ethylene system polymer with which the above ends may denaturalize. It is mixed with a pigment, and then this dispersant is kneaded and combed by the extruder after mixing with covering color resin, is used as a dry color, the Colorcon pound, or a masterbatch, prevents condensation of a pigment, and raises the dispersibility of a pigment more.

[0021] The lubricant for vinyl chloride resin concerning this invention consists of a low-molecular-weight ethylene system polymer with which the above ends may denaturalize. This lubricant is further blended with polyvinyl chloride resin and a heat-resistant stabilizer, and enables lowering and processing which carried out long duration stability further for the kneading torque at the time of processing of extrusion molding etc.

[0022]

[Detailed Description of the Invention] The low-molecular-weight ethylene system polymer concerning this invention is a low-molecular-weight (**) polymer which becomes the single-sided end of a polymer chain from ethylene independence or ethylene, and the alpha olefin of carbon numbers 3-10 including the unsaturated bond of a vinyl mold or a vinylidene mold. As an alpha olefin of carbon numbers 3-10 used for this invention, a propylene, 1-butene, a 3-methyl-1-butene, 1-pentene, a 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, etc. are mentioned, and one sort in these or two sorts or more are used, for example. Also especially in this, a FUPURO pyrene is desirable.

[0023] the low-molecular-weight ethylene system polymer of this invention — an ethylene unit — 81-100-mol % — desirable — 90-100-mol % — especially — desirable — 94-100-mol % — containing — the alpha olefin of carbon

numbers 3-10 — 0-19-mol % — desirable — 0-10-mol % — more — desirable — 0-6-mol % — it contains.

[0024] The limiting viscosity ($[\eta]$) measured in 135 degrees C of the low-molecular-weight ethylene system polymer of this invention and a decalin is 0.01 – 1.7 dl/g, and is 0.01 – 0.4 dl/g more preferably 0.01 to 0.6 dl/g.

[0025] The ratios (M_w/M_n) of the weight average molecular weight (M_w) measured with the gel permeation chromatography (GPC) of the low-molecular-weight ethylene system polymer of this invention and number average molecular weight (M_n) are 1.1–3.0, and are in the range of 1.2–2.5 preferably.

[0026] several vinyl groups per [which was measured by the infrared absorption spectrometry of the low-molecular-weight ethylene system polymer of this invention] 1000 carbon — M and vinylidene — the base — N fills the following relational expression (I).

$$M+N \geq 14000/M_w \text{ (I)}$$

The infrared spectrophotometer (Jasco [Corp.] make: DS-702G) of <infrared-absorption-spectrometry (infrared absorption spectral method)> marketing is used, an about 0.25cm solid-state thin film is created from 0.15cm in thickness by law a heat-and-pressure total using a standard sample, and the infrared absorption spectrum between 850cm⁻¹ is measured from 1000cm⁻¹.

[0027] 1-Aikoh Seng (carbon number 20) is used as <measuring method of number of vinyl groups> model matter, and it checks that the deformation vibration outside a field of this matter is in 910cm⁻¹. Using this absorption band, using the polyethylene which does not include an unsaturated bond with 1-Aikoh Seng, the number of vinyl groups measures the thickness of measurement and a sample for the absorbance of a known sample beforehand, and it asks for the absorbance per unit thickness. A graphic display of the relation between the number of vinyl groups and the absorbance per this unit membrane thickness acquires a linear calibration curve mostly. Therefore, the absorbance per unit membrane thickness of various samples is measured using this calibration curve, and the corresponding number of vinyl groups is called for by using this calibration curve.

[0028] < vinylidene — the calibration curve about the number of the measuring method > above-mentioned vinyl groups of the base and the same calibration curve are created. 2, the 5-dimethyl -1, and 5-hexadiene are used for the model matter in this case. 890cm⁻¹ observed is used for an absorption band.

[0029] As for the low-molecular-weight ethylene system polymer concerning this invention, it is desirable to denaturalize the single-sided end of a polymer chain by an oxygen content radical, a nitrogen content radical, a boron content radical, a sulfur content radical, the Lynn content radical, the silicon content radical, the germanium content radical, the halogen content radical, or the tin content radical. These denaturation objects are approaches as shown in Die Makromolecular Chemie Makromolekular Symposia 48/49, 317–332, and 1991 from the end vinyl or the end vinylidene radical of a polymer chain of a low-molecular-weight polymer, and can denaturalize.

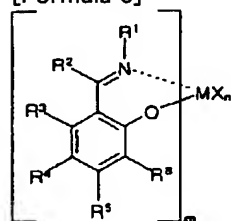
[0030] For example, the oligomer containing oligomer with the oxygen content radical which denaturalized the end by the maleic anhydride, an amide group, and an amine radical etc. is suitable for the coating additive and pigment agent for thixotropy grant etc. Moreover, the oligomer with a silicon content radical, a tin content radical, etc. is suitable for lubricant, such as an application to polyvinyl chloride lubricant, and engineering plastics, a paper processing agent, etc.

[0031] The transition-metals compound expressed with the general formula (II) which carries out (A) after-mentioned of the low-molecular-weight ethylene system polymer concerning this invention, (B) (B-1) Organometallic compound (B-2), organic aluminum oxy compound, It reaches (B-3). According to the catalyst for olefin polymerization characterized by consisting of at least one sort of compounds chosen from the compound which reacts with a transition-metals compound (A) and forms an ion pair It is desirable to manufacture by carrying out the polymerization of ethylene independence or ethylene, and the alpha olefin of carbon numbers 3-10.

[0032] Each catalyst component which forms the catalyst for olefin polymerization used in case the polymer of this invention is manufactured is explained.

(A) Transition-metals compound [0033]

[Formula 3]



... (II)

[0034] (In addition, although having configured is shown, N....M does not have to be made general, even if it has configured in this invention.)

Among a general formula (II), M shows the transition-metals atom (a lanthanoids is also contained in three groups) of the 3-11th groups of a periodic table, is 3 – 9 group's (a lanthanoids is also contained in three groups) metal atom preferably, is the metal atom of 3 – 5 group and nine groups more preferably, and is the metal atom of four groups or five groups especially preferably. Specifically it is a scandium, titanium, a zirconium, a hafnium, vanadium, niobium, a tantalum, cobalt, a rhodium, an yttrium, chromium, molybdenum, a tungsten, manganese, a rhenium, iron, a ruthenium, etc., is a scandium, titanium, a zirconium, a hafnium, vanadium, niobium, a tantalum, cobalt a rhodium, etc. preferably and is titanium, a zirconium, a hafnium, cobalt, a rhodium, vanadium, niobium, a tantalum etc. more

preferably, and they are titanium, a zirconium and hafnium especially preferably.

[0035] m — 1-6 — the integer of 1-4 is shown preferably. Even if R1-R6 are mutually the same, they may differ from each other, they may show a hydrogen atom, a halogen atom, a hydrocarbon group, heterocyclic compound residue, an oxygen content radical, a nitrogen content radical, a boron content radical, a sulfur content radical, the Lynn content radical, a silicon content radical, a germanium content radical, or a tin content radical, may connect it mutually [two or more pieces] of these, and may form the ring.

[0036] A fluorine, chlorine, a bromine, and iodine are mentioned as a halogen atom. As a hydrocarbon group, specifically Methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, neopentyl, carbon atomic numbers, such as n-hexyl, — 1-30 — desirable — the alkyl group; vinyl of the shape of a straight chain of 1-20, and the letter of branching — carbon atomic numbers, such as an allyl compound and isopropenyl, — 2-30 — desirable — the alkenyl radical; ethynyl of the shape of a straight chain of 2-20, and the letter of branching — a carbon atomic number, such as propargyl, — 2-30 — desirable — the alkynyl group; cyclo propyl of the shape of a straight chain of 2-20, and the letter of branching — carbon atomic numbers, such as cyclo butyl, cyclopentyl, cyclohexyl, and adamantyl, — 3-30 — desirable — the cycloalkane radical; cyclopentadienyl of 3-20 — The annular unsaturated hydrocarbon radical of the carbon numbers 5-30, such as indenyl and fluorenyl; Phenyl, Benzyl, naphthyl, a biphenyl, terphenyl, phenan tolyl, carbon atomic numbers, such as anthracenyl, — 6-30 — alkylation aryl groups, such as aryl group; tolyl of 6-20, iso-propyl phenyl, t-butylphenyl, dimethylphenyl, and G t-butylphenyl, etc. are mentioned preferably.

[0037] a hydrogen atom permutes the above-mentioned hydrocarbon group with a halogen — having — **** — for example, the carbon atomic numbers 1-30, such as trifluoromethyl, pentafluorophenyl, and chlorophenyl, — the halogenated hydrocarbon radical of 1-20 is mentioned preferably.

[0038] Moreover, the above-mentioned hydrocarbon group may be permuted by other hydrocarbon groups, for example, aryl group permutation alkyl groups, such as benzyl and cumyl, etc. are mentioned. The above-mentioned hydrocarbon group further again A heterocyclic compound residue; ARUKOSHIKI radical, An aryloxy group, an ester group, a ether group, an acyl group, a carboxyl group, Oxygen content radicals, such as a cull BONATO radical, a hydroxy group, a peroxy group, and a carboxylic anhydride radical; The amino group, An imino group, an amide group, an imide radical, a hydrazino radical, a hydrazono group, a nitro group, A nitroso group, a cyano group, an iso cyano group, a cyanic-acid ester group, an amidino group, Nitrogen content radicals, such as that from which a diazo group and the amino group became ammonium salt; A borane diyl radical, Boron content radicals, such as a borane TORIIRU radical and a JIBORANIRU radical; A sulfhydryl group, A thioester radical, a dithio ester group, an alkylthio group, an aryl thio radical, A thioacyl radical, a thioether radical, a thiocyanate radical, an iso CHIAN acid ester group, A sulphone ester radical, a sulfonamide radical, a thio carboxyl group, a dithio carboxyl group, Sulfur content radicals, such as a sulfonic group, a sulfonyl group, a sulfinyl group, and a sulfenyl radical; you may have the Lynn content radicals, such as a phosphide radical, a phosphoryl group, a thio phosphoryl group, and a phosphato radical, the silicon content radical, the germanium content radical, or the tin content radical.

[0039] Especially among these Methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, neopentyl, the carbon atomic numbers 1-30, such as n-hexyl, — desirable — the alkyl group; phenyl of the shape of a straight chain of 1-20, and the letter of branching — the carbon atomic numbers 6-30, such as naphthyl, a biphenyl, terphenyl, phenan tolyl, and anthracenyl, — desirable — aryl group [of 6-20]; — these aryl groups — a halogen atom — the carbon atomic numbers 1-30 — the alkyl group of 1-20 or an alkoxy group, the carbon atomic numbers 6-30, the permutation aryl group that 1-5 substituents, such as an aryl group of 6-20 or an aryloxy group, permuted preferably are preferably desirable.

[0040] As an oxygen content radical, a nitrogen content radical, a boron content radical, a sulfur content radical, and a Lynn content radical, what carried out [above-mentioned] instantiation, and the same thing are mentioned. As heterocyclic compound residue, a carbon atomic number is mentioned for 1-30, the radical that substituents, such as an alkyl group of 1-20 and an alkoxy group, permuted further preferably to residue and such heterocyclic compound residue, such as sulphur-containing compounds, such as oxygenated compounds, such as nitrogen-containing compounds, such as a pyrrole, a pyridine, a pyrimidine, a quinoline, and triazine, a furan, and a pyran, and a thiophene.

[0041] Specifically as a silicon content radical, a silyl radical, a siloxy radical, a hydrocarbon permutation silyl radical, a hydrocarbon permutation siloxy radical, etc. are mentioned for methyl silyl, dimethylsilyl, trimethylsilyl, ethyl silyl, diethyl silyl, triethyl silyl, diphenyl methyl silyl, triphenyl silyl, dimethylphenyl silyl, dimethyl-t-butylsilyl, dimethyl (pentafluorophenyl) silyl, etc. In these, methyl silyl, dimethylsilyl, trimethylsilyl, ethyl silyl, diethyl silyl, triethyl silyl, dimethylphenyl silyl, triphenyl silyl, etc. are desirable. Trimethylsilyl, triethyl silyl, triphenyl silyl, and dimethylphenyl silyl are especially desirable. Specifically, trimethylsiloxy etc. is mentioned as a hydrocarbon permutation siloxy radical.

[0042] As a germanium content radical and a tin content radical, what permuted the silicon of said silicon content radical by germanium and tin is mentioned. Next, the example of R1-R6 which were explained above is explained more concretely.

[0043] As an alkoxy group, among oxygen content radicals, methoxy and ethoxy **n-propoxy, Isopropoxy, n-butoxy, iso butoxy, tert-butoxy, etc. are mentioned. As an aryloxy group Phenoxy, 2, 6-dimethyl phenoxy, 2 and 4, 6-trimethyl phenoxy, etc. are mentioned. As an acyl group A formyl group, an acetyl group, benzoyl, p-chloro benzoyl, p-methoxy BENSOIRU radical, etc. are mentioned. As an ester group Acetyloxy, benzoyloxy one, methoxycarbonyl, phenoxy carbonyl, p-chloro phenoxy carbonyl, etc. are mentioned.

[0044] As an amide group, as an amino group, an acetamide, N-methyl acetamide, N-methyl benzamide, etc. are mentioned, dimethylamino, ethyl methylamino, diphenylamino, etc. are mentioned, aceto imide, bends imide, etc. are mentioned and methylimino, ethylimino, propyl imino ** butyl imino ** phenylimino, etc. are mentioned as an imino group as an imide radical among nitrogen content radicals.

[0045] As an alkylthio group, among sulfur content radicals A methylthio, ethyl thio, etc. are mentioned. As an aryl thio radical Phenylthio, methyl phenylthio, NARUCHIRUCHIO, etc. are mentioned. As a thioester radical Acetyl thio, benzoyl thio, methylthio carbonyl, phenylthio carbonyl, etc. are mentioned. As a sulphone ester radical Sulfonic-acid methyl, sulfonic-acid ethyl, sulfonic-acid phenyl, etc. are mentioned, and a phenyl sulfonamide, N-methyl sulfonamide, N-methyl-p-toluenesulfonamide, etc. are mentioned as a sulfonamide radical.

[0046] In addition, R6 It is desirable that they are substituents other than hydrogen. Namely, R6 It is desirable that they are a halogen atom, a hydrocarbon group, heterocyclic compound residue, an oxygen content radical, a boron content radical, a sulfur content radical, a silicon content radical, a germanium content radical, or a tin content radical. It is especially R6. It is desirable that they are a halogen atom, a hydrocarbon group, heterocyclic compound residue, a hydrocarbon permutation silyl radical, a hydrocarbon permutation siloxy radical, an alkoxy group, an alkylthio group, an aryloxy group, an aryl thio radical, an acyl group, an ester group, a thioester radical, an amide group, the amino group, an imide radical, an imino group, a sulphone ester radical, a sulfonamide radical, a cyano group, a nitro group, or a hydroxy group, and it is desirable that they are a halogen atom, a hydrocarbon group, and a hydrocarbon permutation silyl radical further.

[0047] R6 ***** — as a desirable hydrocarbon group — methyl, ethyl, and n-propyl — Isopropyl, n-butyl, isobutyl, sec-butyl, and tert-butyl, carbon atomic numbers, such as neopentyl one, tert-amyl, and n-hexyl, — 1-30 — desirable — the alkyl group; cyclo propyl of the shape of a straight chain of 1-20, and the letter of branching — carbon atomic numbers, such as cyclo butyl, cyclopentyl, cyclohexyl, and adamantyl, — 3-30 — desirable — the cycloalkane radical; phenyl of 3-20 — carbon atomic numbers, such as benzyl, naphthyl, biphenyl, and TORIFENIRIRU, — 6-30 — desirable — aryl group [of 6-20]; — and these radicals — a carbon atomic number — 1-30 — desirable — the alkyl group of 1-20, or an alkoxy group — a carbon atomic number — 1-30 — the alkyl halide radical of 1-20 and a carbon atomic number are preferably mentioned for 6-30, the radical that substituents, such as the aryl group of 6-20 or an aryloxy group, a halogen, a cyano group, a nitro group, and a hydroxy group, permuted further preferably.

[0048] R6 It carries out and methyl silyl, dimethylsilyl, trimethylsilyl, ethyl silyl, diethyl silyl, triethyl silyl, diphenyl methyl silyl, triphenyl silyl, dimethylphenyl silyl, dimethyl-t-butylsilyl, dimethyl (pentafluorophenyl) silyl, etc. are mentioned as a desirable hydrocarbon permutation silyl radical. Trimethylsilyl, triethyl phenyl, diphenyl methyl silyl, iso phenyl silyl, dimethylphenyl silyl, dimethyl-t-butylsilyl, dimethyl (pentafluorophenyl) silyl, etc. are mentioned especially preferably.

[0049] At this invention, it is R6. Especially if it carries out, isopropyl, isobutyl, sec-butyl, carbon atomic numbers, such as tert-butyl, neopentyl one, and tert-amyl, — 3-30 — desirable — the letter alkyl group of branching of 3-20 — A carbon atomic number the hydrogen atom of these radicals And 6-30, the radical preferably permuted by the aryl group of 6-20 (cumyl radical etc.), It is desirable that carbon atomic numbers, such as adamantyl, cyclo propyl, cyclo butyl, cyclopentyl, and cyclohexyl, are 3-30, and the radical preferably chosen from the cycloalkane radical of 3-20. Or it is desirable the carbon atomic numbers 6-30, such as phenyl, naphthyl, fluorenyl, anthranil, and phenan tolyl, and that they are also the aryl group of 6-20 or a hydrocarbon permutation silyl radical preferably.

[0050] R1 -R6 The hydrocarbon ring in which 2 or more of radicals of these and the radical which adjoins preferably connect with mutually, and contains different atoms, such as a fat ring, a ring, or a nitrogen atom, may be formed, and these rings may have the substituent further.

[0051] Moreover, R1 -R6 which belongs to one ligand when m is two or more R1 -R6 belonging to other ligands It may be connected. Furthermore, it is R1 when m is two or more. Comrades and R2 Comrades and R3 Comrades and R4 Comrades and R5 Even if comrades and R6 comrades are mutually the same, they may differ.

[0052] the number with which n fills the valence of M — it is — concrete — 0-5 — desirable — 1-4 — it is the integer of 1-3 more preferably. X shows a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen content radical, a sulfur content radical, a nitrogen content radical, a boron content radical, an aluminum content radical, the Lynn content radical, a halogen content radical, heterocyclic compound residue, a silicon content radical, a germanium content radical, or a tin content radical. In addition, when n is two or more, even if mutually the same, you may differ.

[0053] A fluorine, chlorine, a bromine, and iodine are mentioned as a halogen atom. As a hydrocarbon group, what was illustrated by said R1-R6, and the same thing are mentioned. Specifically Methyl, ethyl, propyl, butyl, hexyl, octyl, Alkyl groups, such as nonyl, dodecyl, and eye KOSHIRU; Cyclopentyl, Carbon atomic numbers, such as cyclohexyl, norbornyl, and adamantyl, the cycloalkyl radical; vinyl of 3-30, Alkenyl radicals, such as propenyl and cyclohexenyl; Benzyl, phenylethyl, Arylated alkyl radicals, such as phenylpropyl; although aryl groups, such as phenyl, tolyl, dimethylphenyl, trimethyl phenyl, ethyl phenyl, propyl phenyl, a biphenyl, naphthyl, methyl naphthyl, anthryl, and phenan tolyl, etc. are mentioned It is not limited to these. Moreover, halogenated hydrocarbon and the radical which at least one hydrogen of the hydrocarbon group of the carbon atomic numbers 1-20 permuted by the halogen are also specifically contained in these hydrocarbon groups.

[0054] The thing of 1-20 has [among these] a desirable carbon atomic number. As heterocyclic compound residue, what was illustrated by said R1-R6, and the same thing are mentioned.

[0055] although what was illustrated by said R1-R6, and the same thing are mentioned as an oxygen content radical

and aryl alkoxy group; acetoxy radical; carbonyl groups, such as aryloxy group; phenyl methoxies, such as ARUKOSHIKI radical; phenoxies, such as hydroxy group; methoxy and ethoxy ** propoxy and butoxy one, methylphenoxy, dimethyl phenoxy, and naphthoxy ones, and phenylethoxy, etc. are specifically mentioned, it is not limited to these.

[0056] As a sulfur content radical, what was illustrated by said R1-R6, and the same thing are mentioned. Specifically Methylsulfonate, trifluoromethane sulfonate, phenyl sulfonate, Benzyl sulfonate, p-toluene sulfonate, trimethyl benzene sulfonate, TORIISO butylbenzene sulfonate, p-chlorobenzene sulfonate, Sulfonate radicals, such as pentafluoro benzene sulfonate; Methyl sulfinatate, Sulfinatate group; alkylthio groups, such as phenyl sulfinatate, benzyl SURUFINETO, p-toluenesulfonate, trimethyl benzene sulfinatate, and pentafluoro benzene sulfinatate; although an aryl thio radical etc. is mentioned It is not limited to these.

[0057] Although the specifically same thing as what was illustrated by said R1-R6 is mentioned and an arylamino radical or alkyl arylamino radicals, such as alkylamino radical; phenylamino, such as amino-group; methylamino, dimethylamino, diethylamino, dipropylamino, dibutylamino, and dicyclohexylamino, diphenylamino, ditolylamino, dinaphthylamino, and methylphenylamino, etc. are specifically mentioned as a nitrogen content radical, it is not limited to these.

[0058] Specifically, BR4 (R shows an aryl group, a halogen atom, etc. which may have hydrogen, an alkyl group, and a substituent) is mentioned as a boron content radical. Although phosphite radical (phosphide radical); phosphonic acid radical; phosphinic acid radicals, such as thoria reel phosphine radical; methyl phosphite, such as trialkylphosphine radical; triphenyl phosphine, such as a trimethyl phosphine, tributyl phosphine, and tri-cyclohexyl phosphine, and a tritolyl phosphine, ethylphosphite, and phenyl phosphite, etc. are specifically mentioned as a Lynn content radical, it is not limited to these.

[0059] What was illustrated by said R1-R6, and the same thing are specifically mentioned as a silicon content radical. Specifically Phenyl silyl, diphenyl silyl, trimethylsilyl, triethyl silyl, TORIPURO pill silyl, tricyclohexyl silyl, triphenyl silyl, Methyl diphenyl silyl, tritolyl silyl, hydrocarbon permutation silyl radical [, such as trinaphthyl silyl,]; — hydrocarbon permutation silyl ether group [, such as the trimethylsilyl ether,]; — silicon permutation alkyl group [, such as trimethylsilylmethyl,]; — silicon permutation aryl groups, such as trimethylsilyl phenyl, etc. are mentioned.

[0060] As a germanium content radical, what was illustrated by said R1-R6, and the same thing are mentioned, and, specifically, the radical which permuted the silicon of said silicon content radical by germanium is mentioned.

[0061] As a tin content radical, what was illustrated by said R1-R6, and the same thing are mentioned, and, specifically, the radical which permuted the silicon of said silicon content radical by tin is mentioned.

[0062] Although iodine content radicals, such as chlorine content radicals, such as fluorine content radicals, such as PF6 and BF4, and ClO4, SbCl6, and IO4, are specifically mentioned as a halogen content radical, it is not limited to these.

[0063] Although AIR4 (R shows an aryl group, a halogen atom, etc. which may have hydrogen, an alkyl group, and a substituent) is specifically mentioned as an aluminum content radical, it is not limited to these.

[0064] In addition, when n is two or more, it may join together mutually and two or more radicals which may differ even if two or more radicals shown by X are mutually the same, and are shown by X may form a ring. Although the concrete example of a transition-metals compound expressed with the above-mentioned general formula (II) below is shown, it is not limited to these.

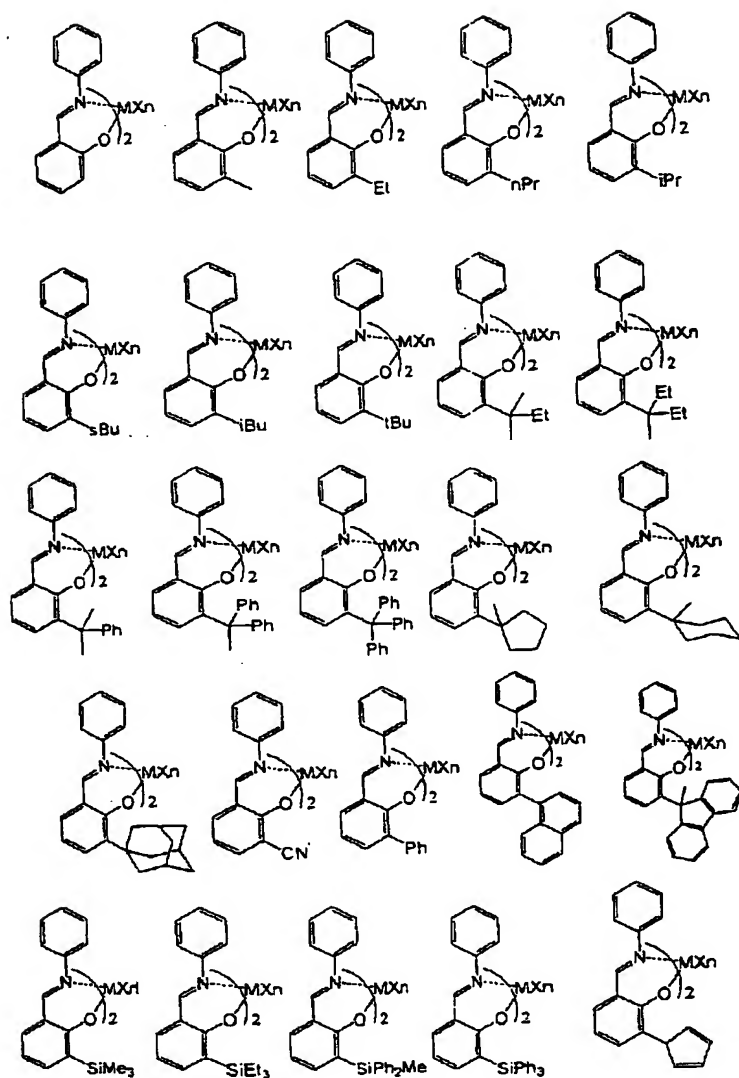
[0065] In the following example, M is a transition-metals element. In addition, separately Sc (III), Ti (III), Ti (IV), Zr (III), Zr (IV), Hf (IV), V (IV), and Nb (V) Ta (V) Although Co (II), Co (III), Rh (II), Rh (III), and Rh (IV) are shown It is not limited to these. In these, it is Ti (IV). Zr (IV) Hf (IV) is desirable and especially Zr (IV) and Hf (IV) are desirable.

[0066] Although X shows alkyl groups, such as halogens, such as Cl and Br, or methyl, it is not limited to these. Moreover, when there is two or more X, even if these are the same, they may differ.

[0067] n is determined by the valence of Metal M. For example, when two sorts of mono-anion kinds have combined with the metal, at divalent metal, it is set to n= 1 in n= 0 and trivalent metal, and is set n= 3 with n= 2 and a pentavalent metal by the quadrivalent metal. For example, when a metal is Ti (IV), it is n= 2, and in the case of Zr (IV), it is n= 2, and, in Hf (IV), is n= 2.

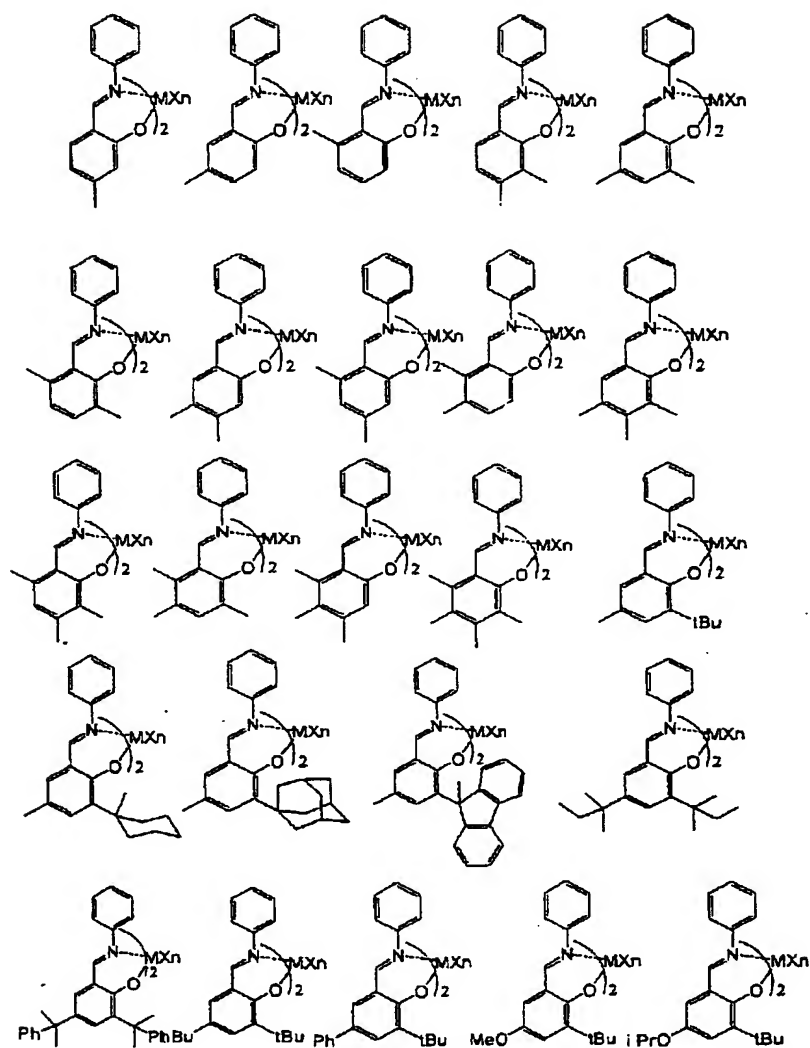
[0068]

[Formula 4]



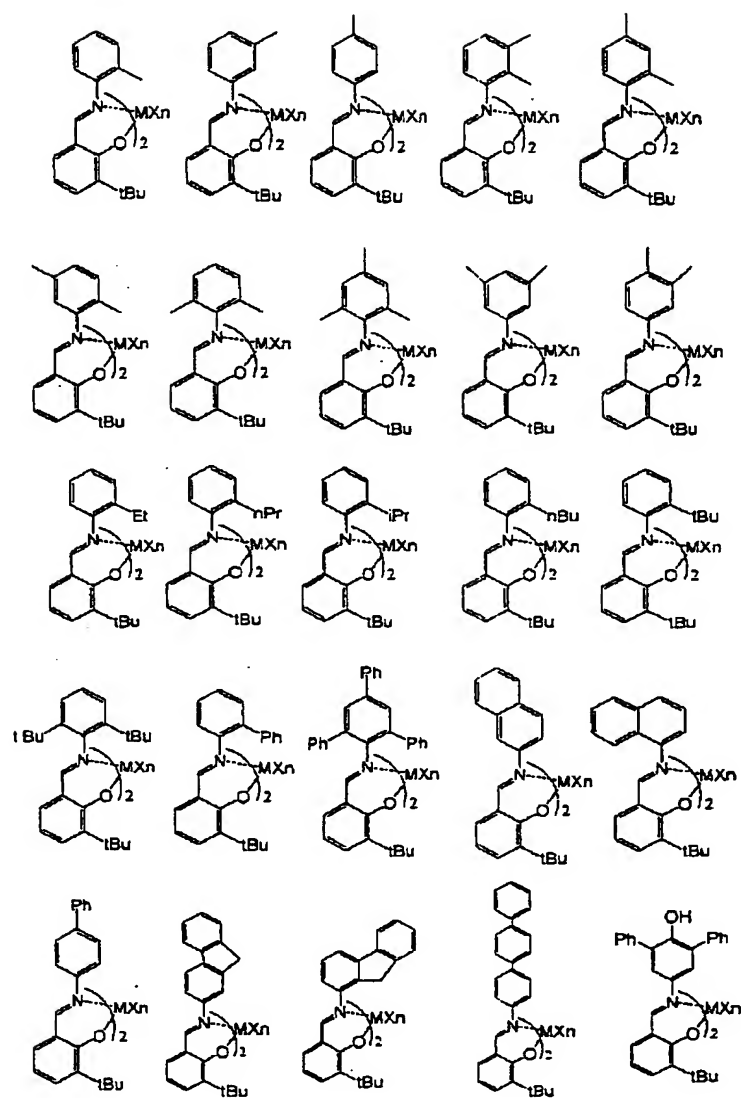
[0069]

[Formula 5]



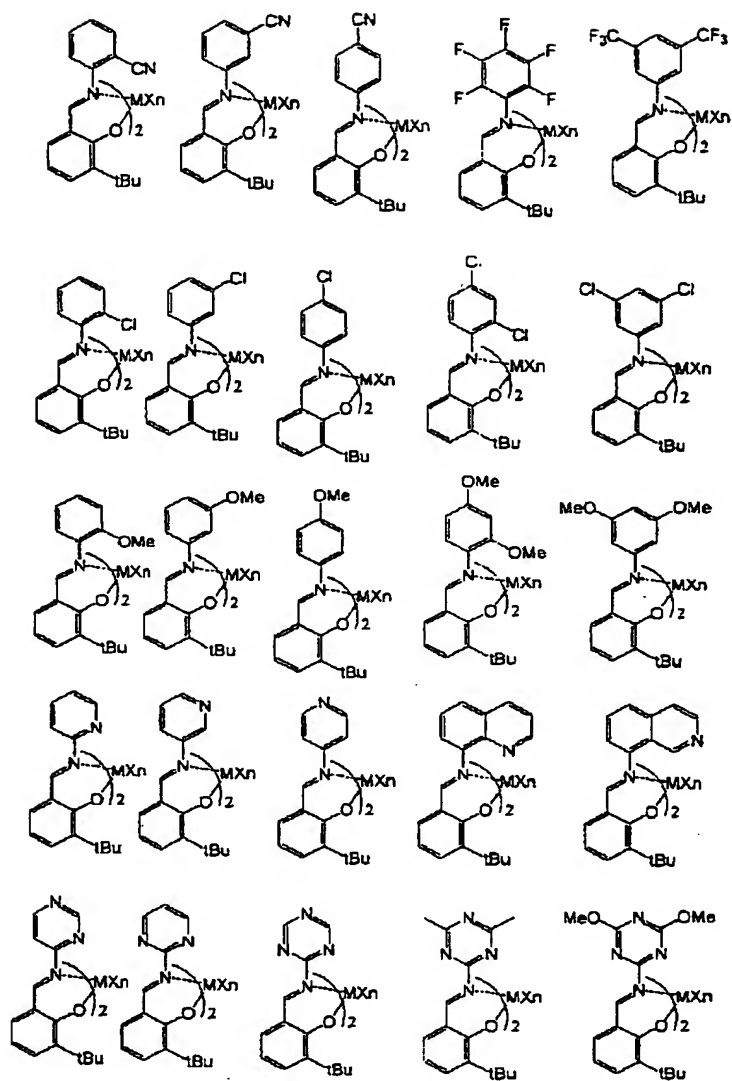
[0070]

[Formula 6]



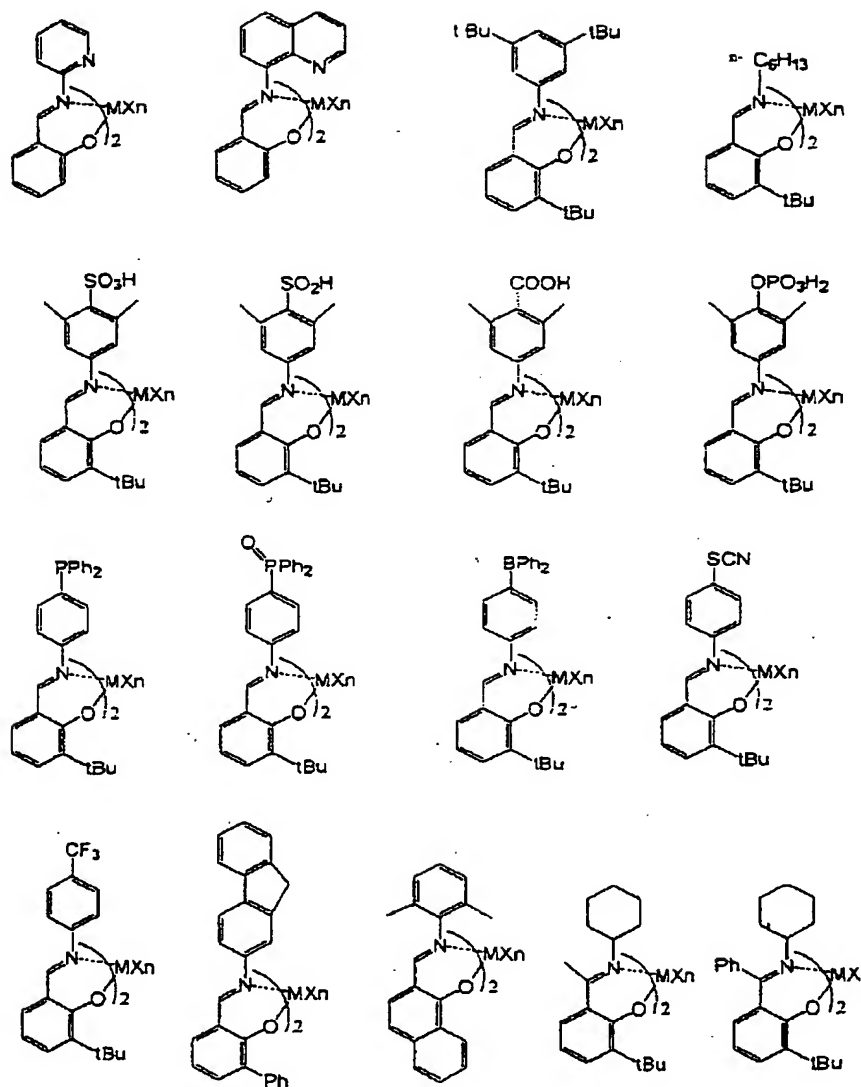
[0071]

[Formula 7]



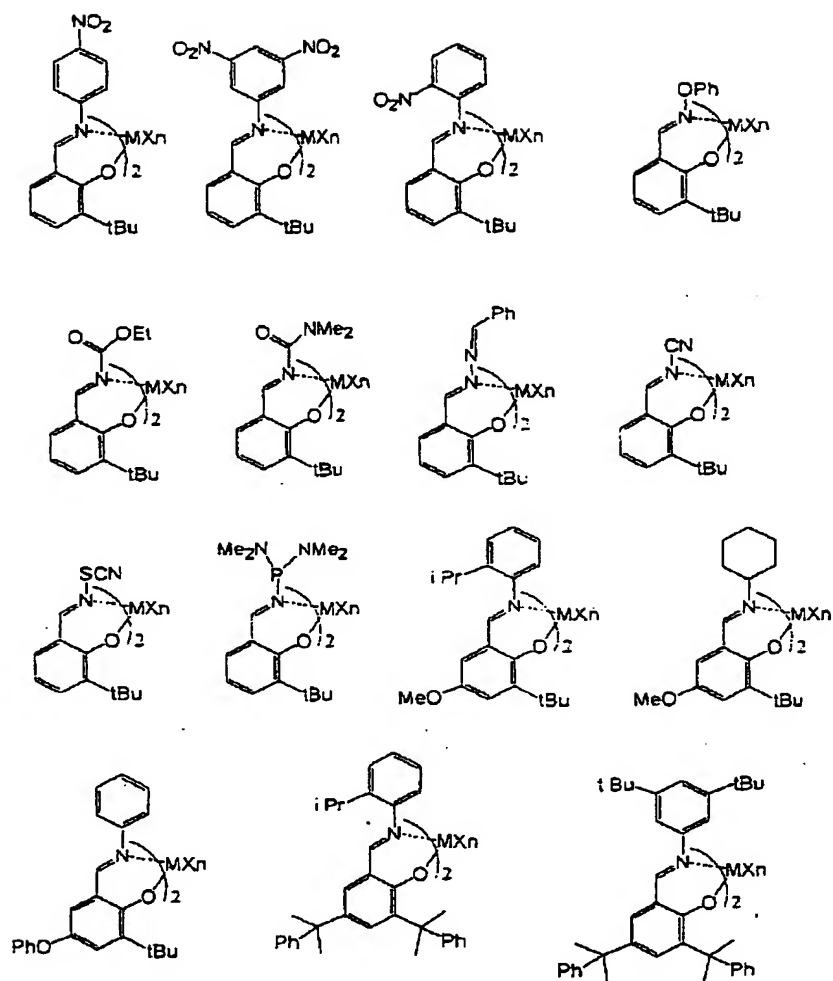
[0072]

[Formula 8]



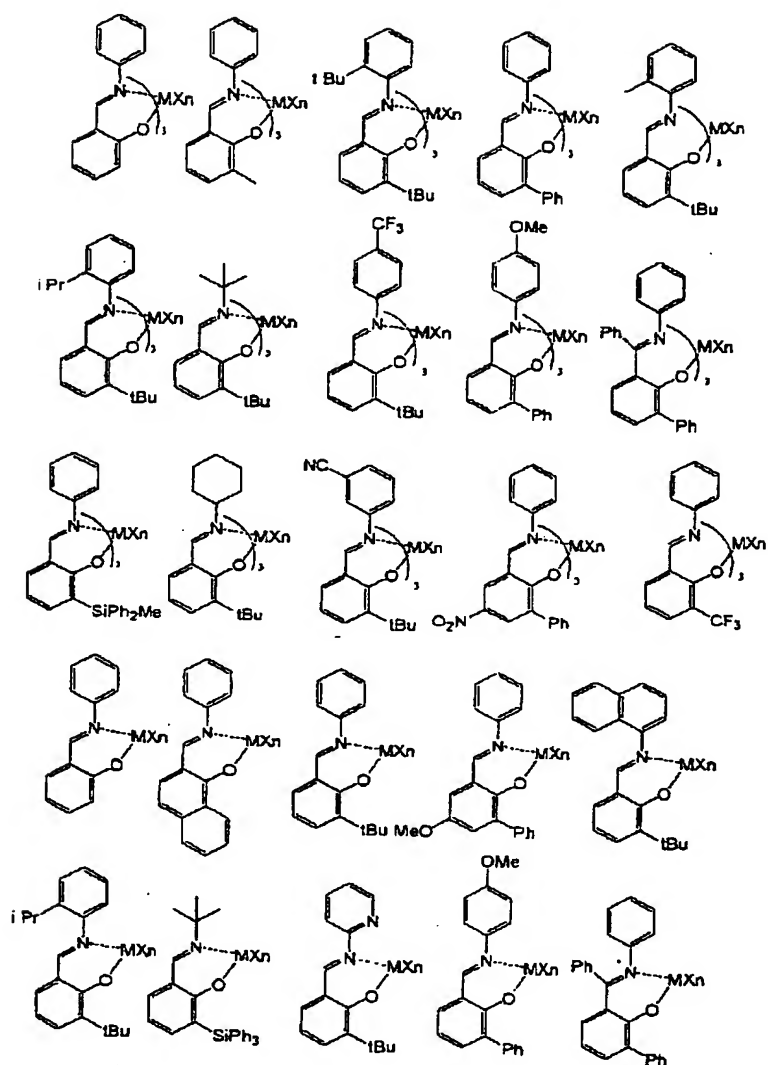
[0073]

[Formula 9]



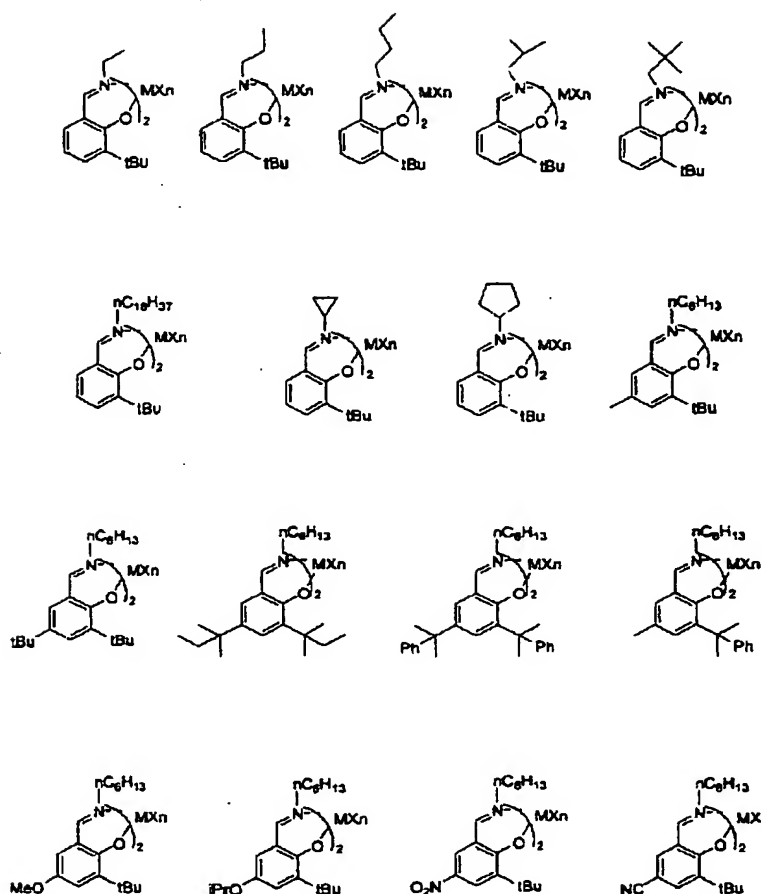
[0074]

[Formula 10]



[0075]

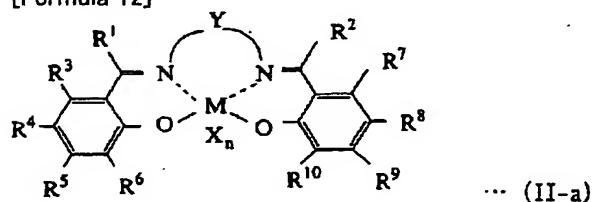
[Formula 11]



[0076] In addition, for an ethyl group and iPr, i-propyl group and tBu are [under the above-mentioned instantiation and Me / a methyl group and Et] tert. - Butyl and Ph show a phenyl group. Moreover, as a (B) transition-metals compound expressed with a general formula (II), there is a transition-metals compound expressed with the following general formula (II-a).

[0077]

[Formula 12]



[0078] (M shows the transition-metals atom of the 3-11th groups of a periodic table among a formula. R1-R10) You may differ, even if mutually the same. A hydrogen atom, a halogen atom, a hydrocarbon group, Heterocyclic compound residue, an oxygen content radical, a nitrogen content radical, a boron content radical, a sulfur content radical, The Lynn content radical, a silicon content radical, a germanium content radical, or a tin content radical is shown, it may connect mutually [two or more pieces] of these, and the ring may be formed. n It is the number which fills the valence of M. X A hydrogen atom, a halogen atom, a hydrocarbon group, An oxygen content radical, a sulfur content radical, a nitrogen content radical, a boron content radical, an aluminum content radical, The Lynn content radical, a halogen content radical, heterocyclic compound residue, a silicon content radical, a germanium content radical, or a tin content radical is shown, and when n is two or more It may join together mutually and two or more radicals which may differ even if two or more radicals shown by X are mutually the same, and are shown by X may form a ring. Y The divalent joint radical containing at least one sort of elements chosen from the group which consists of oxygen, sulfur, carbon, nitrogen, Lynn, silicon, a selenium, tin, and boron is shown, and when it is a hydrocarbon group, it is the radical which consists of three or more carbon numbers.

[0079] a general formula (II-a) — setting — R6 or R10 — at least — on the other hand — especially, it is desirable that both are a halogen atom, a hydrocarbon group, heterocyclic compound residue, an oxygen content radical, a nitrogen content radical, a boron content radical, a sulfur content radical, the Lynn content radical, a silicon content radical, a germanium content radical, or a tin content radical.

[0080] a general formula (II-a) — setting — M and R1- M and R1- which were mentioned about the compound of a

general formula (II) as R10 and X — the same radical as R6 and X can be used. Especially as X, the hydrocarbon group or sulfonate radical of 1-20 has a halogen atom and a desirable carbon atomic number. When n is two or more, the ring which two or more X connects mutually and forms may be an aromatic series ring, or may be an aliphatic series ring.

[0081] Y shows the divalent joint radical containing at least one sort of elements chosen from the group which consists of oxygen, sulfur, carbon, nitrogen, Lynn, silicon, a selenium, tin, and boron as mentioned above, and when it is a hydrocarbon, it is a joint radical which consists of three or more carbon atoms.

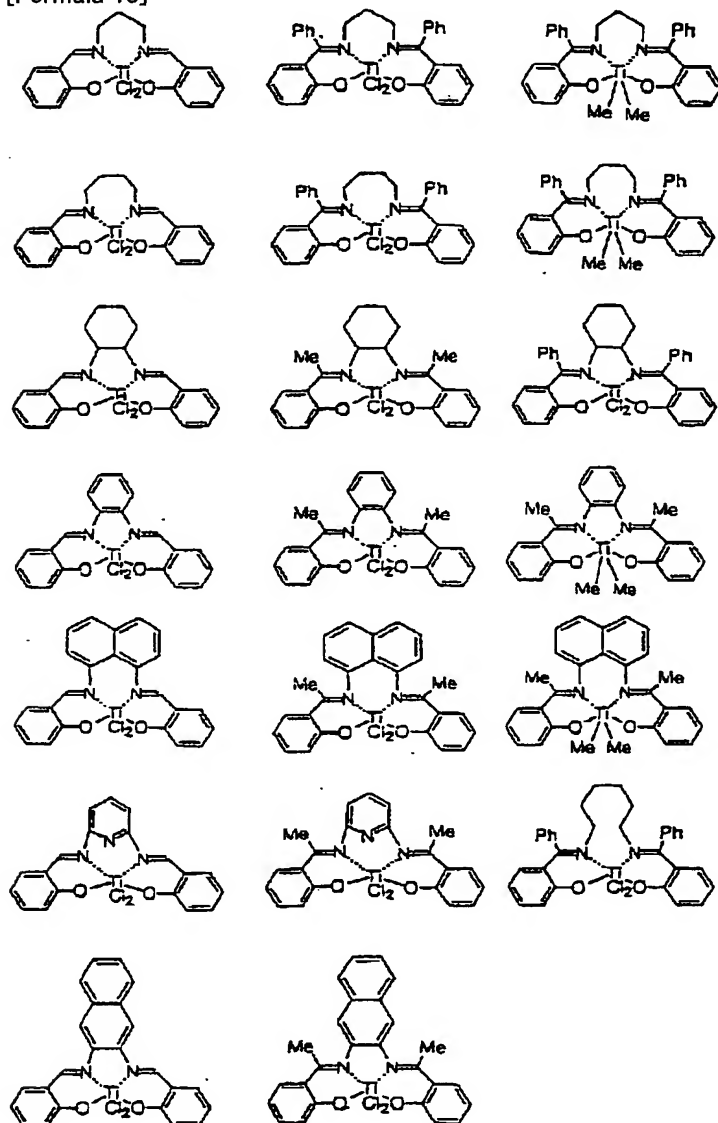
[0082] As for these joint radicals Y, a principal chain has preferably the structure which consisted of four or more pieces [ten or less] preferably especially four or more pieces [20 or less] three or more atoms. In addition, these joint radicals may have the substituent.

[0083] As a divalent joint radical (Y), specifically Chalcogen atom; -NH(s)[, such as -O-, -S- and -Se-,], - Nitrogen, such as N(CH3)-, -PH-, and -P(CH3)-, or Lynn atom content radical; -SiH2-, - Silicon atom content radicals, such as Si(CH3)2-, boron atom content radicals, such as tin atom content radical; -BHs[, such as -SnH2- and -Sn(CH3)2-,], -B(CH3)-, and -BF-, etc. are mentioned. As a hydrocarbon group, carbon atomic numbers, such as -(CH2)4-, -(CH2)5-, and -(CH2)6-, the saturated hydrocarbon radical; cyclohexylidene radical of 3-20, A part of these saturated hydrocarbon radicals Cycloalkane radicals, such as a cyclo hexylene radical; 1-10 hydrocarbon groups, Halogens, such as a fluorine, chlorine, and a bromine, oxygen, sulfur, nitrogen, Lynn, silicon, The radical permuted with hetero atoms, such as a selenium, tin, and boron; Benzene, naphthalene, carbon atomic numbers, such as an anthracene, — residue [of the cyclic hydrocarbon of 6-20]; — the carbon atomic number containing hetero atoms, such as a pyridine, a quinoline, a thiophene, and a furan, is mentioned for the residue of the ring compound of 3-20 etc.

[0084] Although the concrete example of a transition-metals compound expressed with the above-mentioned general formula (II-b) below is shown, it is not limited to these.

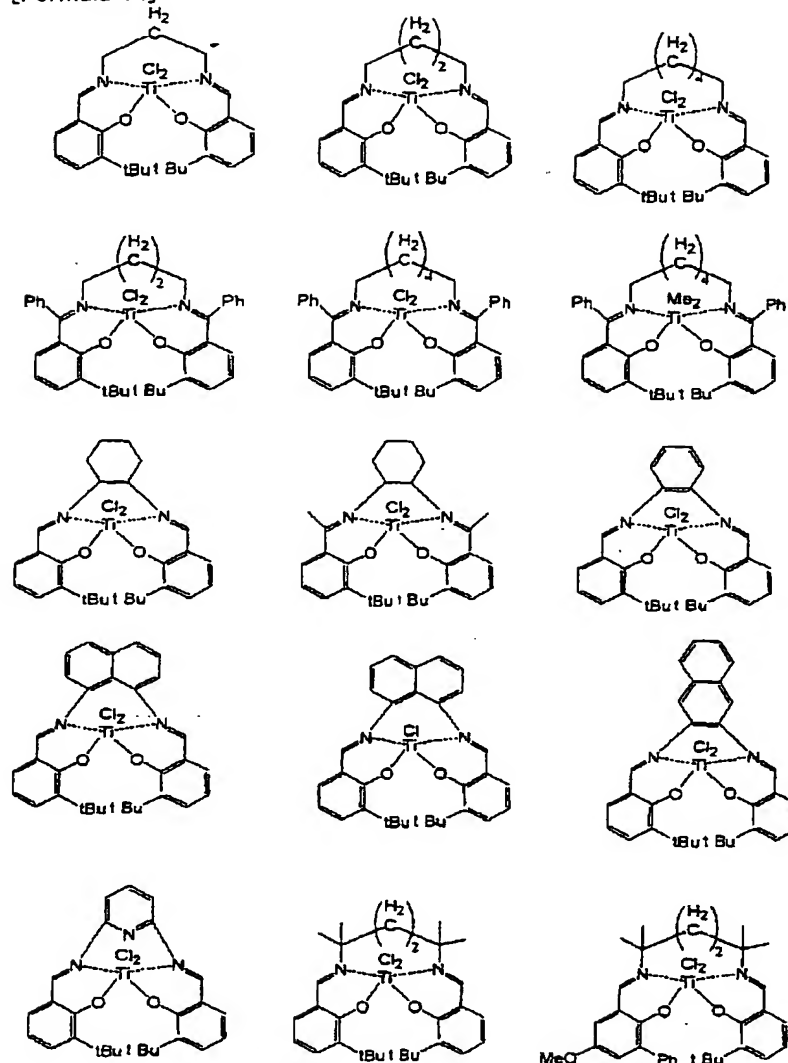
[0085]

[Formula 13]



[0086]

[Formula 14]



[0087] In addition, Me shows a methyl group during the above-mentioned instantiation, and Ph shows a phenyl group. In this invention, the transition-metals compound which transposed the titanium metal to metals other than titanium, such as a zirconium and a hafnium, can also be used in the above compounds.

[0088] (b-1) It is used by organometallic compound this invention (b-1). As an organometallic compound, the organometallic compound of the following periodic-table the 1st and 2 groups and, and the 12th and 13 group is specifically used.

[0089] (b-1a) General formula $RaAl(ORb)_nHpXq$ (Ra and Rb among a formula) even when it is mutually the same — differing — **** — a carbon atomic number — 1-15 — the hydrocarbon group of 1-4 is shown preferably, X shows a halogen atom, $0 < m \leq 3$ and n are $[0 < p < 3$ and q of $0 < n < 3$ and p] the number of $0 < q < 3$, and m is $m+n+p+q=3$. The organoaluminium compound expressed.

[0090] (b-1b) general formula ** alkylation object of the 1st group metal of a periodic table and aluminum which are expressed with $M2AlRa4$ (the inside of a formula, and $M2$ — Li, Na, or K — being shown — Ra — a carbon atomic number — 1-15 — the hydrocarbon group of 1-4 is shown preferably.).

[0091] (b-1c) general formula Dialkyl compound of the 2nd group of the periodic table to whom it is expressed with $RaRbM3$ (even when the inside of a formula, Ra, and Rb are mutually the same — differing — **** — a carbon atomic number — 1-15 — the hydrocarbon group of 1-4 is shown preferably, and $M3$ is Mg, Zn, or Cd.), or the 12th group metal.

[0092] The following compounds etc. can be illustrated as an organoaluminium compound which belongs above (b-1a).

general formula Organoaluminium compound; expressed with $RaAl(ORb)_3-m$ (even when the inside of a formula, Ra, and Rb are mutually the same — differing — **** — a carbon atomic number — 1-15 — the hydrocarbon group of 1-4 is shown preferably, and m is the number of $1.5 \leq m \leq 3$ preferably.)

general formula Organoaluminium compound; expressed with $RaAlX_3-m$ (the inside of a formula, and Ra — a

carbon atomic number — 1-15 — the hydrocarbon group of 1-4 is shown preferably, X shows a halogen atom, and m is $0 < m < 3$ preferably.)

general formula Organoaluminium compound; expressed with $RaAlH_3-m$ (the inside of a formula, and Ra — a carbon atomic number — 1-15 — the hydrocarbon group of 1-4 is shown preferably, and m is $2 < m < 3$ preferably.)

general formula Organoaluminium compound expressed with $RaAl(ORb)_nX_q$ (even when the inside of a formula, Ra, and Rb are mutually the same — differing — **** — a carbon atomic number — 1-15 — the hydrocarbon group of 1-4 is shown preferably, X shows a halogen atom, $0 < n < 3$ and q of $0 < m < 3$ and n are the number of $0 < q < 3$, and m is $m+n+q=3$).

[0093] More specifically as an organoaluminium compound belonging to (b-1a) Trimethylaluminum, Triethylaluminum, Tetraethylaluminum, Tetra-n-butyl aluminum, TORIPURO pill aluminum, Tripentylaluminum, trihexyl aluminum, trioctyl aluminum, Tetra-n-alkylaluminum, such as tridecyl aluminum; Triisopropyl aluminum, Triisobutylaluminum, Tetra sec-butyl aluminum, Tetra tert-butyl aluminum, Tetra 2-methylbutyl aluminum, Tetra 3-methylbutyl aluminum, Tetra 2-methyl pentyl aluminum, Tetra 3-methyl pentyl aluminum, Tetra 4-methyl pentyl aluminum, Tetra 2-methyl hexyl aluminum, Tetra branched chain alkylaluminum, such as Tetra 3-methyl hexyl aluminum and Tetra 2-ethylhexyl aluminum; Tricyclohexyl aluminum, Tricyclo alkylaluminum, such as tricyclo octyl aluminum; Triphenyl aluminum, Tetra phenyl aluminum, such as tritolyl aluminum; dialkyl aluminum hydride; $(i-C_4H_9)_xAl(C_5H_{10})_z$, such as a diisobutyl aluminum hydride (among a formula, x, and y and z are positive numbers and are $z \geq 2x$.) etc. — trialkenylaluminum; isobutyl aluminum methoxides, such as TORIISO prenyl aluminum expressed, — Alkylaluminum alkoxides, such as isobutyl aluminum ethoxide and isobutyl aluminum isopropoxide; A dimethyl aluminum methoxide, Dialkyl aluminum alkoxides, such as diethyl aluminum ethoxide and dibutyl aluminum butoxide; Ethyl aluminum sesquiethoxide, Alkylaluminum sesquialkoxides, such as butyl aluminum sesquibutoxide; The alkylaluminum; diethyl aluminum phenoxide which has the average presentation expressed with $Ra_2.5Al(ORb)_{0.5}$ etc. and by which alkoxy ** was carried out selectively, Diethyl aluminum (2, 6-G t-butyl-4-methyl phenoxide), An ethyl aluminum screw (2, 6-G t-butyl-4-methyl phenoxide), Diisobutyl aluminum (2, 6-G t-butyl-4-methyl phenoxide), Dialkyl aluminum aryl oxide, such as an isobutyl aluminum screw (2, 6-G t-butyl-4-methyl phenoxide); Dimethyl aluminum chloride, A diethylaluminum chloride, dibutyl aluminum chloride, diethyl aluminum bromide, Dialkyl aluminum halide, such as diisobutyl aluminum chloride; Ethylaluminum sesquichloride, Alkylaluminum sesquihalide, such as butyl aluminum sesquichloride and ethylaluminum sesquibromide; Ethyl aluminum dichloride, propyl aluminum dichloride and butyl aluminum — a jib — the alkylaluminum; diethyl aluminum hydride halogenated selectively [alkylaluminum dihalide, such as ROMIDO, etc.] — Dialkylaluminum hydrides, such as a dibutyl aluminum hydride; An ethyl aluminum dihydrido, Alkylaluminum hydrogenated selectively [others, such as alkylaluminum dihydridos, such as a propyl aluminum dihydrido,]; Ethyl aluminum ethoxy chloride, The alkylaluminum which alkoxy-**(ed) and was halogenated selectively [butyl aluminum butoxy chloride, ethyl aluminum ethoxy bromide, etc.] can be mentioned.

[0094] Moreover (b-1a), the organoaluminium compound which could also use the similar compound, for example, two or more aluminium compounds combined through the nitrogen atom can be mentioned. as such a compound — concrete — $2(C_2H_5)_2AlN(C_2H_5)_2$ aluminum $(C_2H_5)_2$ etc. — it can mention.

[0095] as the compound which belongs above (b-1b) — $LiAl(C_2H_5)_4$ and $LiAl(C_7H_{15})_4$ etc. — it can mention. Moreover, in addition to this, it is also alike (b-1), As an organometallic compound, methyl lithium, an ethyl lithium, a propyl lithium, butyl lithium, methyl magnesium bromide, methyl magnesium chloride, ethyl magnesium bromide, ethyl magnesium chloride, propyl magnesium bromide, propyl magnesium chloride, butyl magnesium bromide, butyl magnesium chloride, dimethyl magnesium, diethyl magnesium, dibutyl magnesium, butyl ethyl magnesium, etc. can also be used.

[0096] Moreover, combination with a compound with which the above-mentioned organoaluminium compound is formed within a polymerization system, for example, aluminum halide, and alkyl lithium, or the combination of aluminum halide and alkyl magnesium can also be used.

[0097] (b-1) In an organometallic compound, an organoaluminium compound is desirable. It is above (b-1). An organometallic compound is one-sort independent, or is combined two or more sorts and used.

[0098] (b-2) It is used by organic aluminum oxy compound this invention (b-2). An organic aluminum oxy compound may be an organic aluminum oxy compound of benzene insolubility which may be well-known aluminosilane and is conventionally illustrated by JP,2-78687,A.

[0099] Conventionally, well-known aluminosilane can be manufactured by the following approaches, and is usually obtained as a solution of a hydrocarbon solvent, for example.

(1) How to add organoaluminium compounds, such as trialkylaluminum, to hydrocarbon medium suspension, such as the salts containing the compound containing the water of adsorption, or water of crystallization, for example, a magnesium chloride hydrate, a copper-sulfate hydrate, an aluminum-sulfate hydrate, a nickel-sulfate hydrate, and the 1st cerium hydrate of chlorination, and to make the water of adsorption or water of crystallization, and an organoaluminium compound react to it.

(2) How to make direct water, ice, or a steam act on organoaluminium compounds, such as trialkylaluminum, in media, such as benzene, toluene, ethyl ether, and a tetrahydrofuran.

(3) How to make organic stannic-acid ghosts, such as dimethyl tin oxide and dibutyltin oxide, react to organoaluminium compounds, such as trialkylaluminum, in media, such as Deccan, benzene, and toluene.

[0100] In addition, this aluminosilane may contain a little organic metal component. Moreover, after distilling and removing a solvent or an unreacted organoaluminium compound from the collected solution of the above-mentioned aluminosilane, a solvent may be made to suspend in the poor solvent of remelting or aluminosilane.

[0101] Specifically, the same organoaluminium compound as what was illustrated as an organoaluminium compound which belongs above (b-1a) can be mentioned as an organoaluminium compound used in case aluminosilane is prepared.

[0102] Trialkylaluminum and tricyclo alkylaluminum are desirable and especially trimethylaluminum is [among these] desirable. The above organoaluminium compounds are one-sort independent, or are combined two or more sorts and used.

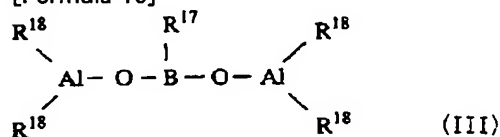
[0103] As a solvent used for preparation of aluminosilane, hydrocarbon solvents, such as halogenide division of petroleum fraction [such as alicyclic group hydrocarbon; gasolines, such as aliphatic hydrocarbon; cyclopentanes such as aromatic hydrocarbon; pentanes, such as benzene, toluene, a xylene, a cumene, and a cymene a hexane, a heptane, an octane, Deccan, a dodecane, hexadecane and OKUTA decane, a cyclohexane, cyclooctane, and methylcyclopentane, kerosene, and gas oil]; and the above-mentioned aromatic hydrocarbon, aliphatic hydrocarbon, and an alicyclic group hydrocarbon, a chlorination object, and a bromination object, are mentioned. Furthermore, ether, such as ethyl ether and a tetrahydrofuran, can also be used. Aromatic hydrocarbon or aliphatic hydrocarbon is desirable especially among these solvents.

[0104] Moreover, the organic aluminum oxy compound of benzene insolubility used by this invention has that desirable whose aluminum component which dissolves in 60-degree C benzene is usually insolubility or poor solubility 5% or less 10% or less to what [what is 2% or less especially preferably], i.e., benzene, preferably in aluminum atom conversion.

[0105] The organic aluminum oxy compound which contained the boron expressed with the following general formula (III) as an organic aluminum oxy compound used by this invention can also be mentioned.

[0106]

[Formula 15]



[0107] As for R¹⁷, a carbon atomic number shows the hydrocarbon group of 1-10 among a formula. You may differ, even if R¹⁸ is mutually the same, and a hydrogen atom, a halogen atom, and a carbon atomic number show the hydrocarbon group of 1-10.

[0108] The organic aluminum oxy compound containing the boron expressed with said general formula (III) is the following general formula (the alkyl boron acid expressed with IV), and R¹⁷-B-(OH)₂ — (IV) (R¹⁷ shows the same radical as the above among a formula.)

An organoaluminium compound can be manufactured in an inert solvent under an inert gas ambient atmosphere by making it react at the temperature of -80 degrees C - a room temperature for 1 minute to 24 hours.

[0109] As a concrete thing of the alkyl boron acid expressed with said general formula (IV), methyl boron acid, ethyl boron acid, isopropyl boron acid, n-propyl boron acid, n-butyl boron acid, isobutyl boron acid, n-hexyl boron acid, cyclohexyl boron acid, phenyl boron acid, 3, 5-difluoro boron acid, pentafluorophenyl boron acid, 3, and 5-screw (trifluoromethyl) phenyl boron acid etc. is mentioned. In these, a methyl boron acid, n-butyl boron acid, an isobutyl boron acid, 3, a 5-difluoro phenyl boron acid, and a pentafluorophenyl boron acid are desirable. These are one-sort independent, or are combined two or more sorts and used.

[0110] Specifically, the same organoaluminium compound as what was illustrated as an organoaluminium compound which belongs above (b-1a) can be mentioned as such an alkyl boron acid and an organoaluminium compound made to react.

[0111] Trialkylaluminum and tricyclo alkylaluminum are desirable and especially trimethylaluminum, triethylaluminum, and triisobutylaluminum are [among these] desirable. These are one-sort independent, or are combined two or more sorts and used.

[0112] It is above. (b-2) An organic aluminum oxy compound is one-sort independent, or is combined two or more sorts and used.

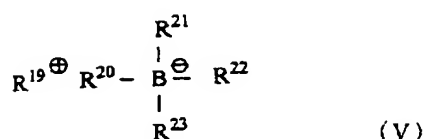
(b-3) The compound (b-3) which reacts with the transition-metals compound (A) used by compound this invention which reacts with a transition-metals compound and forms an ion pair, and forms an ion pair (It is hereafter called an "ionization ionicity compound".) If it carries out, JP,1-501950,A, JP,1-502036,A, JP,3-179005,A, JP,3-179006,A, JP,3-207703,A, The Lewis acid indicated by JP,3-207704,A, USP-5321106 No., etc., an ionicity compound, a borane compound, a carborane compound, etc. can be mentioned. Furthermore, a heteropoly compound and an iso poly compound can also be mentioned.

[0113] Specifically as Lewis acid, it is BR₃ (R). It is the phenyl group or fluorine which may have substituents, such as a fluorine, a methyl group, and a trifluoromethyl radical. The compound shown is mentioned. For example, trifluoro boron, triphenyl boron, Tris (4-fluoro phenyl) boron, tris (3, 5-difluoro phenyl) boron, Tris (4-fluoro methylphenyl) boron, tris (pentafluorophenyl) boron, tris (p-tolyl) boron, tris (o-tolyl) boron, tris (3, 5-dimethylphenyl) boron, etc. are mentioned.

[0114] As an ionicity compound, the compound expressed with the following general formula (V), for example is mentioned.

[0115]

[Formula 16]



[0116] As R¹⁹, H⁺, a carbonium cation, an oxonium cation, an ammonium cation, a phosphonium cation, a cycloheptyltriaryl cation, the ferro SENIUMU cation that has transition metals are mentioned among a formula.

[0117] even when R²⁰-R²³ are mutually the same -- differing -- **** -- an organic radical -- they are an aryl group or a permutation aryl group preferably. Specifically, 3 permutation carbonium cations, such as a triphenyl carbonium cation, the Tori (methylphenyl) carbonium cation, and the Tori (dimethylphenyl) carbonium cation, etc. are mentioned as said carbonium cation.

[0118] As said ammonium cation, specifically A trimethylammonium cation, a triethyl ammonium cation, A TORIPURO pill ammonium cation, a tributyl ammonium cation, Trialkylammonium cations, such as a Tori (n-butyl) ammonium cation; N and N-dimethyl anilinium cation, N and N-diethyl anilinium cation, N, and N- an N [, such as 2, 4, and 6-pentamethylanilinium cation,] and N-dialkyl anilinium cation; JI (isopropyl) ammonium cation -- Dialkyl ammonium cations, such as a dicyclohexyl ammonium cation, etc. are mentioned.

[0119] Specifically, thoria reel phosphonium cations, such as an triphenyl phosphonium cation, the Tori (methylphenyl) phosphonium cation, and the Tori (dimethylphenyl) phosphonium cation, etc. are mentioned as said phosphonium cation.

[0120] As R¹⁹, a carbonium cation, an ammonium cation, etc. are desirable and triphenyl carbonium cation, N, and N-dimethyl anilinium cation, N, and N-diethyl anilinium cation is especially desirable.

[0121] Moreover, as an ionicity compound, trialkyl permutation ammonium salt, N, and N-dialkyl anilinium salt, dialkyl ammonium salt, a thoria reel HOSUFONIUMU salt, etc. can also be mentioned.

[0122] As trialkyl permutation ammonium salt, specifically For example, triethyl ammonium tetrapod (phenyl) boron, TORIPURO pill ammonium tetrapod (phenyl) boron, Tori (n-butyl) ammonium tetrapod (phenyl) boron, trimethylammonium tetrapod (p-tolyl) boron, Trimethylammonium tetrapod (o-tolyl) boron, Tori (n-butyl) ammonium tetrapod (pentafluorophenyl) boron, TORIPURO pill ammonium tetrapod (o, p-dimethylphenyl) boron, Tori (n-butyl) ammonium tetrapod (m and m-dimethylphenyl) boron, Tori (n-butyl) ammonium tetrapod (p-trifluoro methylphenyl) boron, Tori (n-butyl) ammonium tetrapod (3, 5-ditrifluoromethyl phenyl) boron, Tori (n-butyl) ammonium tetrapod (o-tolyl) boron, etc. are mentioned.

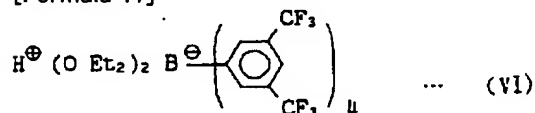
[0123] as N and N-dialkyl anilinium salt -- concrete -- for example, N and N-dimethyl anilinium tetrapod (phenyl) boron, N, and N-diethyl anilinium tetrapod (phenyl) boron, N, and N- 2, 4, and 6-pentamethylanilinium tetrapod (phenyl) boron etc. is mentioned.

[0124] JI (1-propyl) ammonium tetrapod (pentafluorophenyl) boron, dicyclohexyl ammonium tetrapod (phenyl) boron, etc. are specifically as dialkyl ammonium salt mentioned.

[0125] Furthermore, triphenylcarbeniumtetrakis(pentafluorophenyl)borate, N, and N-dimethyl anilinium tetrakis (pentafluorophenyl) borate, ferro SENIUMU tetrapod (pentafluorophenyl) borate, triphenyl KARUBENIUMUPENTA phenyl cyclopentadienyl complex, N, and N-diethyl anilinium PENTAFENIRU cyclopentadienyl complex, the following type (VI), or (VII) the boron compound expressed can also be mentioned as an ionicity compound.

[0126]

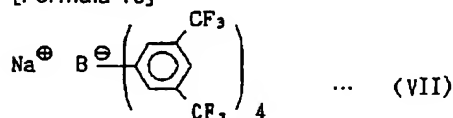
[Formula 17]



[0127] (Et shows an ethyl group among a formula.)

[0128]

[Formula 18]



[0129] As a borane compound, specifically For example, decaborane (14); screw [Tori (n-butyl) ammonium] nona borate, Screw [Tori (n-butyl) ammonium] deca borate, screw [Tori (n-butyl) ammonium] undeca borate, Screw [Tori (n-butyl) ammonium] dodeca borate, screw [Tori (n-butyl) ammonium] deca chloro deca borate, The salt of anions, such as screw [Tori (n-butyl) ammonium] dodeca chloro dodeca borate; Tori (n-butyl) ammonium screw (dodeca hydride dodeca borate) cobalt acid chloride (III), The salt of metal borane anions, such as screw [Tori (n-butyl) ammonium] screw (dodeca hydride dodeca borate) nickel acid chloride (III), etc. is mentioned.

[0130] As a carborane compound, specifically For example, 4-cull BANONA borane (14), 1, 3-JIKARUBA nona borane (13), 6, 9-JIKARUBA decaborane (14), The dodeca hydride-1-phenyl -1, 3-JIKARUBA nona borane, The dodeca hydride-1-methyl -1, 3-JIKARUBA nona borane, undecahydride -1, the 3-dimethyl -1, 3-JIKARUBA nona borane, 7, 8-JIKARUBA undeca borane (13), 2, 7-JIKARUBA undeca borane (13), Undecahydride -7, the 8-dimethyl

-7, 8-JIKARUBA undeca borane, The dodeca hydride-11-methyl -2, 7-JIKARUBA undeca borane, Tori (n-butyl) ammonium 1-cull BADEKA borate, Tori (n-butyl) ammonium 1-KARUBA undeca borate, Tori (n-butyl) ammonium 1-KARUBA dodeca borate, Tori (n-butyl) ammonium 1-trimethylsilyl-1-cull BADEKA borate, Tori (n-butyl) ammonium BUROMO-1-KARUBA dodeca borate, Tori (n-butyl) ammonium 6-cull BADEKA borate (14), Tori (n-butyl) ammonium 6-cull BADEKA borate (12), Tori (n-butyl) ammonium 7-KARUBA undeca borate (13), Tori (n-butyl) ammonium 7, 8-dicarba undecaborate (12), Tori (n-butyl) ammonium 2, 9-dicarba undecaborate (12), The Tori (n-butyl) ammonium dodeca hydride-8-methyl -7, 9-dicarba undecaborate, Tori (n-butyl) ammonium undecahydride-8-ethyl -7, 9-dicarba undecaborate, Tori (n-butyl) ammonium undecahydride-8-butyl -7, 9-dicarba undecaborate, The Tori (n-butyl) ammonium undecahydride-8-allyl compound -7, 9-dicarba undecaborate, Tori (n-butyl) ammonium undecahydride-9-trimethylsilyl -7, 8-dicarba undecaborate, The salt of anions, such as Tori (n-butyl) ammonium undecahydride -4 and 6-dibromo-7-KARUBA undeca borate; Tori (n-butyl) ammonium screw (nona hydride -1, 3-JIKARUBA nona borate) cobalt acid chloride (III), A Tori (n-butyl) ammonium screw (undecahydride -7, 8-dicarba undecaborate) ferrate (III), Tori (n-butyl) ammonium screw (undecahydride -7, 8-dicarba undecaborate) cobalt acid chloride (III), Tori (n-butyl) ammonium screw (undecahydride -7, 8-dicarba undecaborate) nickel acid chloride (III), Tori (n-butyl) ammonium screw (undecahydride -7, 8-dicarba undecaborate) cuprate (III), A Tori (n-butyl) ammonium screw (undecahydride -7, 8-dicarba undecaborate) aurate (III), A Tori (n-butyl) ammonium screw (nona hydride -7, 8-dimethyl -7, 8-dicarba undecaborate) ferrate (III), A Tori (n-butyl) ammonium screw (nona hydride -7, 8-dimethyl -7, 8-dicarba undecaborate) chromate (III), Tori (n-butyl) ammonium screw (TORIBUROMOOKUTA hydride -7, 8-dicarba undecaborate) cobalt acid chloride (III), A tris [Tori (n-butyl) ammonium] screw (undecahydride-7-KARUBA undeca borate) chromate (III), A screw [Tori (n-butyl) ammonium] screw (undecahydride-7-KARUBA undeca borate) manganate (IV), Screw [Tori (n-butyl) ammonium] screw (undecahydride-7-KARUBA undeca borate) cobalt acid chloride (III), The salt of metal carborane anions, such as screw [Tori (n-butyl) ammonium] screw (undecahydride-7-KARUBA undeca borate) nickel acid chloride (IV), etc. is mentioned.

[0131] The heteropoly compound consists of an atom chosen from silicon, Lynn, titanium, germanium, an arsenic, and tin, and one sort or two sorts or more of atoms chosen from vanadium, niobium, molybdenum, and a tungsten. Specifically Lynn vanadium acid, Germano vanadium acid, arsenic vanadium acid, Lynn niobic acid, Germano niobic acid, a SHIRIKONO molybdic acid, molybdophosphoric acid, A titanium molybdic acid, the Germano molybdic acid, an arsenic molybdic acid, a tin molybdic acid, A tungstophosphoric acid, the Germano tungstic acid, a tin tungstic acid, Phosphorus molybdo vanadium acid, a phosphorus tongue SUTOBANAJINN acid, the Germano TANGUSUTOBANAJINN acid, Phosphorus molybdo TANGUSUTO vanadium acid, Germano molybdo TANGUSUTO vanadium acid, On the metal of the salt of a periodic table of a phosphorus molybdo tungstic acid, phosphorus molybdo niobic acid, and these acids, for example, the 1st group, and two groups, and a concrete target It is not this limitation although organic salt with a salt with a lithium, sodium, a potassium, a rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, etc., a triphenyl ethyl salt, etc. can be used.

[0132] It is above. (b-3) An ionization ionicity compound is one-sort independent, or is combined two or more sorts and used. In the case of a polymerization, although the usage of each component and addition sequence are chosen as arbitration, the following approaches are illustrated.

[0133] (1) Component (A) (B-1), Organometallic compound (B-2), How to add at least one sort of components (B) (only henceforth "a component (B)") chosen from an organic aluminum oxy compound and (B-3) an ionization ionicity compound to curing units in order of arbitration.

[0134] (2) How to add a component (A), the catalyst component for which the component (B-1) was contacted beforehand, and a component (B-3) to curing units in order of arbitration.

(3) How to add the catalyst component for which the component (A) and the component (B-1) were contacted beforehand, and a component (B-1) and a component (B-3) to curing units in order of arbitration. In this case, even if a component (B-1) is the same, they may differ.

[0135] (4) How to add the catalyst component for which the component (A), the component (B-1), and the component (B-3) were contacted beforehand, and a component (B-1) to curing units in order of arbitration. In this case, even if a component (B-1) is the same, they may differ.

[0136] (5) How to add the catalyst for which the component (A) and the component (B-2) were contacted beforehand to curing units.

(6) How to add a component (A) and a component (B-2) to curing units in order of the catalyst component contacted beforehand and a component (B-1), or (B-2) arbitration. In this case, even if a component (B-2) is the same, they may differ.

[0137] In this invention, a polymerization can be carried out also in any of liquid phase polymerization methods, such as a dissolution polymerization and a suspension polymerization, or a vapor-phase-polymerization method. As an inert hydrocarbon medium used in a liquid phase polymerization method, halogenated hydrocarbon or such mixture, such as aromatic hydrocarbon; ethylene chloride, such as alicycle group hydrocarbon; benzene, such as aliphatic hydrocarbon; cyclopentanes, such as a propane, butane, a pentane, a hexane, a heptane, an octane, Decan, a dodecane, and kerosene, a cyclohexane, and methylcyclopentane, toluene, and a xylene, chlorobenzene, and dichloromethane, etc. can be mentioned, and, specifically, the olefin itself can also be used as a solvent.

[0138] It faces performing the polymerization of an olefin using the above catalysts for olefin polymerization, and 10-12 to ten - two mols (A) of components are usually used in an amount which becomes 10-10 to ten - three mols preferably.

[0139] Component (b-1) Component (b-1) A mole ratio [(b-1) /M] with the transition-metals atom (M) in a

component (A) is usually used in 0.01–100000, and an amount that is preferably set to 0.05–50000. Component (b-2) The mole ratio [(b-2) / M] of the aluminum atom in a component (b-2) and the transition-metals atom (M) in a component (A) is usually used in 10–500000, and an amount that is preferably set to 20–100000. Component (b-3) Component (b-3) A mole ratio [(b-3) / M] with the transition-metals atom (M) in a component (A) is usually used in 1–20, and an amount that is preferably set to 1–10.

[0140] Moreover, the range of –50→+200 degrees C of polymerization temperature of the olefin using such a catalyst for olefin polymerization is usually 0–170 degrees C preferably. the polymerization preassure force — usually — ordinary pressure –100 kg/cm² — desirable — ordinary pressure –50 kg/cm² It is under a condition and a polymerization reaction can be performed also in which approach of a batch process, half-continuous system, and continuous system. It is also possible to divide a polymerization into two or more steps where reaction conditions differ, and to perform it furthermore.

[0141] The release agent for toners concerning this invention consists of a low-molecular-weight ethylene system polymer with which the end concerning this invention may denaturalize. This release agent is used as a component of the toner for electrostatic-charge image development with an electrification control agent etc. binding resin (a), a coloring agent (b), and if needed. the number average molecular weight of this release agent — the range of 300 thru/or 2000 — it is the range of 400 thru/or 1000 preferably.

[0142] If it consists of thermoplastics generally blended to the development material of an electrostatic-charge image, any will be sufficient as the above-mentioned binding resin (a), and it will not be restricted especially. For example, what consists of styrene resin, a styrene-acrylic ester acid copolymer, acrylic resin, styrene-butadiene resins, ketone resin, maleic resin, polyester resin, polyvinyl acetate resin, cumarone resin, phenol resin, silicone resin, polyurethane, an epoxy resin, terpene resin, a polyvinyl butyral, poly butyl methacrylate, a polyvinyl chloride, polyethylene, polypropylene, polybutadiene, an ethylene-vinylacetate copolymer, rosin resin, etc. is mentioned. A styrene-acrylic ester copolymer with fixable [sufficient], polyester aromatic series resin, and especially an epoxy resin are desirable at softening temperature (90 degrees C – 120 degrees C) suitable in these.

[0143] If generally blended to the development material of an electrostatic-charge image, any will be sufficient as the coloring agent of the above (b), and it will not be restricted especially. For example, a pigment or colors, such as carbon black, copper-phthalocyanine-blue, aniline-bule, ARUKO oil blue, chrome yellow, ultra marine blue, quinoline yellow, lamp black, rose-bengal, diazo yellow, Rhodamine B lake, and carmine 6B and the Quinacridone derivative, are mentioned, and even when these are independent one sort, even if they combine two or more sorts, they are used.

[0144] The ratios of the release agent of binding resin / coloring agent / electrification control agent / this invention are about 100/10 / 5 / 0.5 to 40 in a weight ratio, and the blending ratio of coal of the release agent for toners of this invention is usually 100/6 / 2 / 20 preferably. [1–6] [0.5–2] [10–20] [1–10] [0–5]

[0145] The pigment agent concerning this invention consists of a low-molecular-weight ethylene system polymer with which the end concerning this invention may denaturalize. After mixing with a pigment and then mixing with covering color resin, this dispersant is kneaded and corned with an extruder, and is used as a dry color, the Colorcon pound, or a masterbatch.

[0146] the blending ratio of coal of the above-mentioned pigment agent — the pigment 100 weight section — receiving — usually — 25 thru/or the 200 weight sections — it is the range of 50 thru/or the 150 weight sections preferably. The range of number average molecular weight is 1000 thru/or 5000, and the range of it is 1500 thru/or 3000 preferably.

[0147] As covering color resin which can be used, polyethylene, polypropylene, polybutene –1, polybutene –1, the Pori 4-methyl pentene –1, ethylene propylene rubber, Polyolefine system resin, such as an ethylene-vinylacetate copolymer, polystyrene, Styrene resin, such as ABS, the polycarbonate resin obtained from bisphenol A and a phosgene, Thermosetting resin, such as thermoplastics, such as polyester resin, such as polyethylene terephthalate and polybutylene terephthalate, polyamide resin, polyphenylene oxide resin, and a polyvinyl chloride, and phenol resin, and an epoxy resin, can be mentioned.

[0148] Especially, the pigment agent of this invention can be suitably used to thermoplastics. The pigment which can be used can be used for all the pigments known by coloring of synthetic resin from the former. When it illustrates concretely as a pigment, metal; calcium carbonates, such as aluminum, silver, and gold, Carbonates, such as a barium carbonate; Oxide;aluminum2O3andnH2O, such as ZnO and TiO2, Hydroxides, such as Fe2O3andnH2O; nitrates [, such as sulfate;Bi(OH)2NO3], such as CaSO4 and BaSO4 ;P Chlorides, such as bCl2; [Chromite, such as chromate;CoCrO(s)4, such as CaCrO4 and BaCrO4,] A manganate and permanganate; — uranates [, such as borate;Na2U2O7.6H2O, such as Cu (BO)2,]; — nitrites [, such as K3Co(NO2) 6.3H2O,]; — silicate [, such as SiO2,]; — *****, such as CuAsO3 and Cu (OH)2, — and **** acid chloride; — acetate [, such as Cu (C2H3O2)2 and Cu (OH)2,]; (NH4) — phosphate [, such as 2MnO2(P2O7) 2,]; — aluminum acid chloride — Molybdate, a zincate, an antimonate, a tungstate selenide, Inorganic pigments, such as a titanate, cyanidation iron salt, phthalate, and CaS, ZnS, CdS, Natural organic pigments, such as a cochineal lake and a MADA lake, naphthol Green Y Nitroso pigments, such as naphthol Green B; Naphthol Yellow S, nitro pigment [, such as pigment chlorin 2G,]; — permanent red 4R; — Hansa Yellow — Azo pigments, such as brilliant carmine 68 and Scarlett 2R; MARAKAIN Green, Basic dye lakes, such as Rhodamine B, acid one, the Green lake, Acid-dye lakes, such as an eosine lake, an alizarin lake, a purpurin lake, Organic pigments, such as phthalocyanine pigments, such as vat dye pigments, such as which mordant dye lake, the thioindigo red B, and intern Indanthrene Orange, a copper phthalocyanine blue, and Phthalocyanine Green, etc. are mentioned.

[0149] Although the pigment agent of this invention is applicable also to coloring by the approach of coloring by the dry color method, the coloring by the Colorcon pound method or the coloring by the masterbatch method either, it can be especially used for the masterbatch method preferably.

[0150] The lubricant for polyvinyl chloride resin concerning this invention consists of a low-molecular-weight ethylene system polymer with which the end concerning this invention may denaturalize. In the polyvinyl chloride constituent using the lubricant of this invention, the blending ratio of coal of lubricant is the range of the 0.05 weight sections thru/or 5 weight sections to the polyvinyl chloride 100 weight section, and is the 0.1 weight section thru/or 3 weight sections preferably. Moreover, number average molecular weight is in the range of 400 thru/or the 4000 weight sections, the polymer used as lubricant is the range of 500 thru/or the 1000 weight sections preferably, further, in using the denaturation object which denaturalized the end, the acid number of this denaturation object is in the range of 2 thru/or 70, and it is the range of the acid numbers 10-50 preferably. When the acid number of a denaturation object is 70 or more, the initial slippage of lubricant falls and the adhesive prevention effectiveness falls or less by ten. Moreover, the adhesive prevention effectiveness as opposed to a metal in the number average molecular weight of lubricant is inferior, and slippage falls by the first stage and the anaphase at large or more by 4000 400 or less. Moreover, in the loadings rate of lubricant, the slippage effectiveness runs short, above 5 weight sections, slippage becomes superfluous and plasticization of a constituent becomes difficult below at the 0.05 weight sections.

[0151] In order to use the above-mentioned denaturation object as lubricant, the single-sided end vinyl group of the polymer chain of a low-molecular-weight ethylene system polymer or vinylidene radical content oligomer concerning this invention as a monomer which denaturalizes Unsaturated carboxylic acid or its anhydride is mentioned. Specifically An acrylic acid, a methacrylic acid, a maleic acid, a maleic anhydride, a citraconic acid, An anhydrous citraconic acid, a fumaric acid, an itaconic acid, itaconic acid anhydride, 3-cyclohexene carboxylic acid, 4-cyclohexene carboxylic acid, 5-norbornene-2, 3-dicarboxylic acid, etc. can be mentioned.

[0152] It puts and the polyvinyl chloride resin containing the polyvinyl chloride resin additive of this invention cannot be used, even if it mixes polyethylene, polypropylene, ABS plastics, MBS resin, an ethylene-vinylacetate copolymer, polymethylmethacrylate, etc. to a polyvinyl chloride or a polyvinyl chloride. Moreover, a heat-resistant stabilizer may be further blended with these constituents.

[0153] If a stabilization effect is shown to polyvinyl chloride resin as a heat-resistant stabilizer which can be used, anything, it will be good, for example, such mixture, such as a lead compound, cadmium compounds, a barium compound, a lime compound, a zinc compound, an organotin compound, an epoxy compound, and KIRETA, will be used.

[0154] The polyvinyl chloride constituent containing this invention lubricant may contain the lubricant of further others, a bulking agent, a pigment, the color, the plasticizer, the antistatic agent, and the weathering stabilizer. Since initial slippage is excellent, the adhesiveness over a metal is mitigated and the constituent containing the lubricant concerning this invention can be fabricated to stability, can cross continuous running to a long time, and can perform it.

[0155] The low-molecular-weight ethylene system polymer concerning this invention can be widely used for the application for which well-known low molecular weight polyethylene, such as a wax, is used. In this case, various additives can also be added and used if needed. For example, if the low-molecular-weight ethylene system polymer concerning this invention is used as a coating modifier, a paint film front face can be reformed, for example, it can excel in lusterless effectiveness, and the abrasion resistance of a paint film can be raised, a high-class feeling can be given to a carpenter coating and endurance can be raised.

[0156] Moreover, if the low-molecular-weight ethylene system polymer concerning this invention is used as polish, such as car wax and a floor polish, it can excel in gloss and paint film physical properties can be raised.

[0157] The low-molecular-weight ethylene system polymer concerning this invention is suitable as a release agent for resin shaping, can give a mold-release characteristic to thermoplastics or thermosetting resin, and can raise a molding cycle.

[0158] The low-molecular-weight ethylene system polymer concerning this invention is excellent in compatibility with rubber, gives a mold-release characteristic to rubber, when it is suitable as rubber processing aid which carries out viscosity control and uses as rubber processing aid, it raises the dispersibility of a filler and a pigment, and since it gives a mold-release characteristic and a fluidity to rubber, it can raise the molding cycle at the time of rubber shaping, and an extrusion property.

[0159] the quality of paper to which the low-molecular-weight ethylene system polymer concerning this invention improves the slippage of paper, and surface treatment — as an improver — suitable — quality of paper — when it uses as an improver, dampproofing, gloss, surface hardness, blocking resistance, and abrasion resistance can be raised, a high-class feeling can be given to paper and endurance can be raised.

[0160] The low-molecular-weight ethylene system polymer concerning this invention can raise the abrasion resistance on the front face of ink, and thermal resistance, when it is suitable as a wear-resistant improver for ink and uses as a wear-resistant improver. The low-molecular-weight ethylene system polymer concerning this invention is suitable as a textile finishing assistant, and when resinating fiber and it uses as a textile finishing assistant, it can give flexibility and slippage to fiber.

[0161] The low-molecular-weight ethylene system polymer concerning this invention is suitable as a hot melt additive, and can give thermal resistance and a fluidity to hot melt adhesive. The quality of the hot melt adhesive in the field as which the thermal resistance of an automobile, building materials, etc. is required can be raised. The

low-molecular-weight ethylene system polymer concerning this invention is suitable as an electric insulation agent, for example, can raise the electric insulation of a film capacitor, and a heat-resistant target. The low-molecular-weight ethylene system polymer concerning this invention is suitable as a compounding agent to natural waxes, such as a crayon and a candle, and can raise surface hardness and softening temperature.

[0162]

[Effect of the Invention] Since the low-molecular-weight ethylene system polymer of this invention has the unsaturated bond of the vinyl mold which has reactivity at the single-sided end of a polymer chain, or a vinylidene mold, it can give the functional group of arbitration by the various denaturation technique.

[0163] Such a polymer and its denaturation object can offer the toner release agent in which the elevated-temperature mold-release characteristic was excellent in, and low-temperature fixable one was excellent. Moreover, said polymer and its denaturation object can offer the pigment agent excellent in pigment dispersibility.

[0164] Furthermore, said polymer and its denaturation object can offer the lubricant for polyvinyl chloride resin excellent in initial slippage.

[0165]

[Example] Hereafter, although this invention is explained still more concretely based on an example, this invention is not limited to these.

[0166] In addition, in this example, limiting viscosity ($[\eta]$) was measured in 135 degrees C and a decalin. molecular weight distribution (Mw/Mn) — the Millipore Corp. make — it measured as follows using GPC-150.

[0167] TSK whose column sizes are the diameter of 27mm, and die length of 600nm as a separation column GNH Using HT, column temperature was made into 140 degrees C, the mobile phase was developed by part for 1.0ml/, using 0.025 % of the weight (Takeda Chemical) of BHT(s) as o-dichlorobenzene (Wako Pure Chem) and an antioxidant, sample concentration was made into 0.1 % of the weight, the sample injection rate was made into 500 microliter, and the differential refractometer was used as a detector. The thing by TOSOH CORP. was used for standard polystyrene.

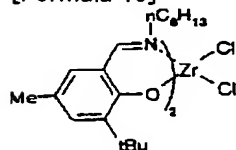
[0168] It substituted asking for the acid number for the quantum of end carbonyl. A potassium-hydroxide neutralization process is used for the acid number, and it is JIS. It applied to K-5902 correspondingly.

[0169]

[The synthetic example 1] Hexane 1L was inserted in the autoclave made from SUS of content volume 2L which fully carried out the nitrogen purge. Subsequently, after carrying out temperature up of the temperature in a system to 120 degrees C, the polymerization was started by pressing methyl aluminoxane 1.25mmol and compound (A-1) 0.001mmol fit with ethylene. By supplying ethylene continuously after that, total pressure was kept at 30kg/cm² and the polymerization was performed for 15 minutes at 120 degrees C. Unreacted ethylene was purged after suspending a polymerization by adding a small amount of methanol in a system. The polymer was deposited by throwing in the obtained polymer solution in the methanol of an overlarge. Filtration recovered the polymer and reduced pressure drying was carried out at 80 degrees C for 10 hours. Consequently, limiting viscosity $[\eta]$ is 0.11 dl/g and polyethylene oligomer 55.2g the number of Mn is [1.9 and the number of vinyl groups per 1000 carbon / g] 14.6 for 900 and Mw/Mn was obtained.

[0170]

[Formula 19]



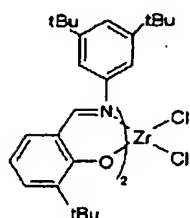
化合物 (A - 1)

[0171]

[The synthetic example 2] At the room temperature, heptane 850ml was inserted in 2made from SUS L autoclave which fully enough carried out the nitrogen purge, and temperature up was carried out to it to 50 degrees C. Then, the propylene was inserted in until the pressure was set to 5.5kg/cm²G, keeping at 50 degrees C, and it pressurized with ethylene until total pressure was further set to 8kg/cm²G. Then, 0.001mmol(s) were pressed fit for methyl aluminoxane 1.25mmol and a compound (A-2), and the polymerization was started. The polymerization was performed at 50 degrees C for 15 minutes, supplying ethylene continuously. The unreacted monomer was purged, after adding a small amount of methanol and suspending a polymerization. The obtained polymer solution was thrown into the methanol of an overlarge, and the polymer was deposited. Filtration recovered the obtained polymer and reduced pressure drying was carried out at 130 degrees C for 10 hours. consequently, limiting viscosity $[\eta]$ — 0.40 dl/g — it is — a propylene content — 4.5-mol% and Mn — 1600 and Mw/Mn — the vinyl group per 1.9 and 1000 carbon, and vinylidene — oligomer 36.5g whose base is 7.2 pieces was obtained.

[0172]

[Formula 20]



化合物 (A-2)

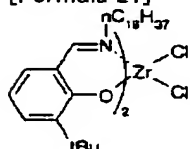
[0173]

[The synthetic example 3] [denaturation of an end unsaturated bond] — oligomer 25g obtained in the synthetic example 2 and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 0.41g were inserted in the 100ml autoclave made from SUS which fully carried out the nitrogen purge, and it agitated at 230 degrees C for 5 hours. Then, maleic anhydride which dissolved 5.9g and tetramethylpiperidine nitro oxide 3mg are inserted in, and 5kg/cm²G was pressurized and it was made to react for 20 minutes with nitrogen. After the sample had dissolved, it took out small quantity every, and it supplied in the cyclohexane of an overlarge, and insoluble matter was removed by filtration. After carrying out reduced pressure distilling off of the cyclohexane in filtrate, reduced pressure drying of the obtained residue was carried out at 100 degrees C for 10 hours. Consequently, 25.5g of denaturation objects which carried out maleic-anhydride denaturation of the end was acquired. [0174]

[The synthetic example 4] At the room temperature, heptane 850ml was inserted in 2made from SUS L autoclave which fully enough carried out the nitrogen purge, and temperature up was carried out to it to 50 degrees C. Then, the propylene was inserted in until the pressure was set to 5.5kg/cm²G, keeping at 50 degrees C, and it pressurized with ethylene until total pressure was further set to 8kg/cm²G. Then, 0.001mmol(s) were pressed fit for methyl aluminoxane 1.25mmol and a compound (A-3), and the polymerization was started. The polymerization was performed at 50 degrees C for 15 minutes, supplying ethylene continuously. The unreacted monomer was purged, after adding a small amount of methanol and suspending a polymerization. The obtained polymer solution was thrown into the methanol of an overlarge, and the polymer was deposited. Filtration recovered the obtained polymer and reduced pressure drying was carried out at 130 degrees C for 10 hours. consequently, limiting viscosity $[\eta]$ — 0.20 dl/g — it is — a propylene content — 3.8-mol% and Mn — 2300 and Mw/Mn — the vinyl group per 2.0 and 1000 carbon, and vinylidene — oligomer 28.7g whose base is 5.5 pieces was obtained.

[0175]

[Formula 21]



化合物 (A-3)

[0176]

[The synthetic example 5] the denaturation which carried out maleic-anhydride denaturation of the end as a result of processing like the synthetic example 3 using the oligomer obtained in the example 4 of [denaturation of end unsaturated bond] composition — 23.1g of adults was obtained. [0177]

[A table 1]

合成したPEオリゴマーの基本物性

	Mw	Mn	Mw/Mn	1000炭素当りの ビニル基数 (個/ [C])	アセチレン 含量 (mol%)	酸価 mgKOH /g
合成例 1	1700	900	1.9	14.6	—	—
合成例 2	3000	1600	1.9	7.2	4.5	—
合成例 3	—	—	—	—	—	20
合成例 4	4600	2300	2.0	5.5	3.8	—
合成例 5	—	—	—	—	—	17

[0178]

[Example 1] The resin (Mitsui Chemicals, Inc. make, CPR-100) 87 section for binders, and the carbon black (MA100; Mitsubishi Chemical make) 8.0 section, The electrification regulator (BONTRON S-34; ORIENT chemical-industry company make) 1.0 section, cooling after setting it as 120 degrees C and kneading using the biaxial kneading machine after carrying out preliminary mixing of the polyethylene oligomer 5.0 section compounded in the synthetic example 1 with a Henschel mixer, and coarse grinding — it pulverized, and classified by the sizer further and the 6.0-18.0-micrometer toner was obtained. Subsequently, the hydrophobic silica (R-972, product made from Aerosil) was added from the outside at a rate used as 0.4 % of the weight to the above-mentioned toner, this was mixed with the Henschel mixer, and the toner was obtained. As a result of evaluating the toner obtained by the above, 135 degrees C and the offset generating temperature (B) of the minimum fixation temperature (A) were 240 degrees C

or more.

[0179] These assessment approaches were performed as follows.

After creating a non-established image with the copying machine which changed suitably the electrophotography copying machine of the minimum fixation temperature (A) marketing, the fixation section of the copying machine of marketing of this non-established image was fixed using the heat roller anchorage device changed suitably. The fixation rate with a heat roller was made into 210 mm/sec, it changed 5 degrees C of temperature of a heat roller at a time, and the toner was established. Covered the obtained fixation image for the 0.5kg load with the sand rubber (dragonfly pencil company make), it was made to rub 10 times, and the friction test was performed. The image concentration before and behind this friction test was measured with a Macbeth style reflection density meter. The rate of change of the image concentration in each temperature considered as the minimum fixation temperature with the minimum fixation temperature used as 70% or more. In addition, the heat roller anchorage device used here does not have a silicone oil feeder style. Moreover, the environmental condition was made into ordinary temperature ordinary pressure (temperature of 22 degrees C, 55% of relative humidity).

[0180] Assessment of offset-proof [offset generating (temperature B)] nature was performed according to measurement of the above-mentioned minimum fixation temperature. That is, after creating a non-established image with the above-mentioned copying machine, the toner image was imprinted and the above-mentioned heat roller anchorage device performed fixation processing. Subsequently, the transfer paper of a blank paper was sent to the heat roller anchorage device concerned under the same conditions, and actuation which carries out visual observation of whether toner dirt arises on a transfer paper was performed. This actuation was repeated two or more times, carrying out sequential lifting of the laying temperature of the heat roller of said heat roller anchorage device. It considered as offset generating temperature with the minimum laying temperature which the dirt by the toner produced. Moreover, the environmental condition was made into ordinary temperature ordinary pressure (temperature of 22 degrees C, 55% of relative humidity).

[0181]

[Example 2] Having impalpable-powder-ized the oligomer obtained in the synthetic example 3 with the desk grinder (50% particle size of 80 micrometers), having dissolved at 180 degrees C, and kneading the copper-phthalocyanine-blue 100 weight section to this, it added gradually and the spherical kneading object with a radius of about 2.5cm was obtained. This kneading solid was supplied to 130-degree C 3 roll **** machine, and the regurgitation rate was calculated from that pass time and discharge quantity. Furthermore, this kneading constituent and polystyrene (the product made from Japanese Polystyrene, trade name TOPO REXX which are called GPPS), or ABS (tic [Sumitomo Chemical Co., Ltd. make and class / MH]) was supplied to 20mmphi extruder which is 230 degrees C and is rotating [ABS / degrees C / 190 / and] at the rate of 50rpm about GPPS at a rate from which the pigment concentration in a kneading moldings becomes 1wt%, and the masterbatch was obtained after kneading. Extrusion nature was evaluated by carrying out the visual judgment of the homogeneity of the surface state of the strand at this time, and the diameter of a strand.

[0182] Moreover, about the transparency of a pigment agent and a masterbatch film, using the masterbatch which uses GPPS as a base material, press working of sheet metal was carried out under conditions with a press temperature of 190 degrees C, and the 0.1mm masterbatch film was obtained. The pigment agent in this masterbatch film was measured with the image-processing machine (the Toyo Ink make, Luzex450). Moreover, the turbidity of the obtained film was measured as film haze. A thing with this smaller value has better transparency.

[0183] The assessment result was as follows.

Film engine-performance pigment dispersibility: The particle number of 50 micrometers or less is 1.00x10³. An individual / two or less cm Hayes : Three 25% workability roll regurgitation rate: 0.085 g/min. extrusion nature : All at the time of using GPPS or ABS are fitness [0184].

[Example 3] 90 degrees C of oligomer 1 weight sections obtained in the polyvinyl chloride (product [made from Ocean Vinyl chloride], trade name TH-1000, degree of polymerization = 1000) 100 weight section, the dioctyl tin JIMERUKAPUTAIDO (trade name OT-4, product made from Tokyo Fine chemical) 2.5 weight section, and the synthetic example 5 were mixed with the Henschel mixer for 3 minutes. The obtained mixture was kneaded with 2 rolls and slippage was evaluated. Measuring time amount until supply a sample between rolls, a charge sample fuses, it becomes sheet-like and it coils around a roll estimated the gelation time. The sample was supplied to the roll, the roll was suspended after mixing for 2 minutes, and observing the ease of exfoliating of the sheet 5, 10, 15, 20, and 30 minutes after after a roll halt estimated the adhesion prevention effectiveness to a roll. This result displayed as x the thing for which ** and exfoliation are improper for the good thing of detachability in a table 2. [thing / O and / which cannot exfoliate easily] In addition, roll actuation was performed on condition that the following.

Diameter of a roll : 8 inch skin temperature : 190-195-degree-C roll spacing : The number of 0.4mm roll revolutions: 18rpm / 20rpm (a front roll / back roll)

The amount of samples: A result is shown in a table 2 once [150 / g/].

[0185]

[A table 2]

滑剤	ゲル化時間 (秒)	ロールからの剝離性				
		5分	10分	15分	20分	30分
合成例5	18	○	○	○	○~△	○~△

[Translation done.]